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MINTEQ User's Manual

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Pacific Northwest Laboratory

Prepared for
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Commission

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ABSTRACT

This MINTEQ user's manual was written to aid the user in applying the MINTEQ geochemical computer code to model aqueous solutions and the interactions of aqueous solutions with hypothesized assemblages of solid phases. The purpose of the user's manual is twofold: 1) to provide a basic understanding of how the MINTEQ computer code operates and the important principles that are incorporated into the code and 2) to instruct a user of the MINTEQ code on how to create input files to simulate a variety of geochemical problems. Chapters 2 through 8 are directed toward the user who has some experience with or wishes to review the principles important to geochemical computer codes. Also contained in these chapters is information on the methodology MINTEQ uses to incorporate these principles into the code. Chapters 9 through 11 are directed toward the user who wants to know how to create input data files to model various types of problems.

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EXECUTIVE SUMMARY

A user's manual was written to assist users of the MINTEQ geochemical computer code in applying the code to modeling aqueous solutions and the interactions of aqueous solutions with hypothesized, solid-phase assemblages. The objective of the MINTEQ user's manual is to provide a basic understanding of the operation of the MINTEQ computer code and important principles that are incorporated into the code. Additionally, and foremost, this manual will instruct the user of the MINTEQ code on how to create input files to simulate a variety of geochemical problems.

The MINTEQ geochemical computer code was constructed by Felmy, Girvin and Jenne of the Pacific Northwest Laboratory, who tried to combine the best features of its two immediate predecessors, MINEQL and WATEQ. The computer code MINTEQ was developed to apply fundamental principles of thermodynamics to solve geochemical equilibria. The computations are performed using an aqueous speciation-solubility-adsorption model. MINTEQ can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas-phase equilibria, and precipitation/dissolution of solid phases. Moreover, MINTEQ can accept a finite mass for any solid considered for dissolution. Therefore, MINTEQ will continue to calculate the dissolution of specified solid phases only until the initial solid-phase masses are exhausted. Sample input files were created to demonstrate how to set up each of the above types of calculations. When needed, we have gone into detail on the theory behind the various types of calculations.

Current publications, "MEXAMS" and "MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria" contain technical information on MINTEQ but only a limited amount of detailed information on setting up input files to perform geochemical calculations. In response to this need, we have produced a MINTEQ user's manual as a guide to performing specific geochemical calculations. This manual will help ensure that the MINTEQ geochemical computer code is properly used when performing these calculations.

CHAPTER 1

INTRODUCTION

The MINTEQ geochemical computer code was developed by Felmy et al. (1984b). MINTEQ integrates many of the capabilities of the WATEQ (Ball et al. 1981) and MINEQL (Westall et al. 1976) codes that are advantageous in modeling studies. MINTEQ can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. Moreover, MINTEQ can accept a finite mass for any solid considered for dissolution and will dissolve the specified solid phase only until its initial mass is exhausted.

Current publications on MINTEQ include "MEXAMS" and "MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria" (Felmy et al. 1984a, 1984b). These publications contain technical information on MINTEQ but only a limited amount of detailed information on setting up input files to perform specific geochemical calculations; hence, the need for a user's manual.

In response to this need, Pacific Northwest Laboratory (PNL) contracted with the Nuclear Regulatory Commission (NRC) to produce a MINTEQ user's manual as a guide to performing specific geochemical calculations. The purpose of the MINTEQ user's manual is twofold: 1) to provide a basic understanding of how the MINTEQ computer code operates and the important principles that are incorporated into the code and 2) to instruct a user of the MINTEQ code on how to create input files to simulate a variety of geochemical problems. The manual will address these points as outlined. Chapters 2 through 8 are directed toward those who wish to review or have limited familiarity with principles important to geochemical computer codes. Also contained in these chapters is information on the methodology MINTEQ uses to incorporate these principles into the code. Chapters 9 through 11 are directed toward the user who wants to know how to create input data files to model various types of problems.

CHAPTER 2

TERMINOLOGY

To clarify the meaning of terms used in this document, brief definitions are given for a few words that may connote different things to different people.

A distinction needs to be made between chemical models of aqueous systems and aqueous/solid systems and the computer codes that execute calculations based on those models. The terms "chemical model," "geochemical model," and "conceptual chemical model" will have the same meaning and refer to a theoretical construct that allows one to predict the specified properties of a system. For example, a hypothetical solid-phase assemblage can be used to represent the interactions of a groundwater with a natural heterogeneous sediment. Often, the predicted properties will be constrained by thermodynamic equilibria. A "computer code" or "computer program" will refer to the sequence of statements written in computer language (e.g., FORTRAN, PASCAL, BASIC, etc.) that solves the mathematical constraints imposed by the chemical model of the system. Thus, the phrase computer code will also refer to the relationships that are expressed in computer language. For example, computer code refers to the relationship between activities and activity coefficients expressed in the code. "Modeling" will be used to refer to the execution of the mathematical calculations based on the chemical model of the system. In other words, the term "modeling" or "model," when used as a verb, will address the integration of the chemical model and the computer code. Sometimes the chemical model of the system will only consist of the chemical models embedded in the MINTEQ code, such as the chemical model based on the ion association theory.

"Validation," as used in this report, will refer to the coherence, to some acceptable accuracy, of laboratory and field data with the predictions made with the chemical model developed for a particular system. The chemical model of a particular system is used in conjunction with a computer code to perform the simulations. We use "verification" to mean that the coding and mathematical algorithms in the computer code were certified to be correct. This verification can be performed by comparing the results obtained from the code with results from other verified codes. Alternatively, one could check the computations performed by the code by hand.

CHAPTER 3

GEOCHEMISTRY REVIEW FOR MINTEQ USERS

The computer code MINTEQ was developed to apply fundamental principles of thermodynamics to solve geochemical equilibria. The computations are performed using an aqueous speciation-solubility-sorption model. The thermodynamic principles on which MINTEQ is based are discussed in this chapter, with particular emphasis on their application to the MINTEQ code.

The physical domain over which a geochemical problem is defined is called a thermodynamic system. MINTEQ was designed to solve geochemical equilibria for systems composed of one kilogram of water, various amounts of material dissolved in solution, and any solid materials that are present. Systems that are modeled using MINTEQ can exchange energy and material (open systems) or just energy (closed systems) with the surrounding environment.

Each system is composed of a number of phases. Every phase is a region of the system with distinct composition and physically definable boundaries. All of the material in the aqueous solution forms one phase. The gas phase is composed of any gaseous material present in the system. Each compositionally and structurally distinct solid forms a separate phase.

The components are the distinct chemical entities of which all of the phases are composed; each phase contains some amount (possibly zero) of each of the components. Each set of components is a linearly independent set that spans the system. In other words, no component can be created from a balanced chemical reaction using the other components, and all of the derived species (aqueous complexes, solids, etc.) in the system can be created from the components. In theory, the choice of components is arbitrary; any complete, linearly independent set can be used. In practice, a particular set of components is defined by the MINTEQ data base, and all of the geochemical equilibria are written in terms of these components. In addition to water, most of the components in the MINTEQ data base are the simplest form of the cations and anions (e.g., Ca^{2+}, Na^{+}, Cl^{-}, CO_3^{2-}, SO_4^{2-}). Usually, the authors of the MINTEQ thermodynamic data base have tried to use the dominant aqueous species over the normal pH range of water as the component. Because the bare ion is not always the dominant species, some components are not formulated in terms of the bare ion; for example, H_4SiO_4 is used in place of Si^{4+}. A list of the components for which thermodynamic data are available in the MINTEQ data base is given in Chapter 9, Table 9.1. Not all of these components and associated thermodynamic data may be available in the particular version of the thermodynamic data base you are using. These components are also known as Type 1 species in the MINTEQ code.

The number of degrees of freedom of the system is the number of system variables (i.e., temperature, pressure, and the masses of each of the components) that can be independently varied. The phase rule relates the number of components, phases, and degrees of freedom of a system at equilibrium. In the MINTEQ code, the temperature and pressure are fixed, and the appropriate form of the phase rule is

$$f = c - p \tag{3.1}$$

where f is the number of degrees of freedom, c is the number of components, and p is the number of phases. For an aqueous system with no solid phases, the number of degrees of freedom is one less than the number of components (recall that the activity of water, one of the components, is fixed). Each solid phase added to the equilibrium assemblage removes one degree of freedom from the system. In addition, each constraint imposed on the system, such as fixed pH, pe, or the activity of another component, reduces the number of degrees of freedom by one. (These constraints are termed Type 3 species in MINTEQ.) Because the minimum number of degrees of freedom for a system is zero, the maximum number of phases that can coexist at equilibrium is equal to the number of components. MINTEQ makes use of the phase rule by eliminating one degree of freedom (i.e., the concentration of one component) for each solid phase in equilibrium with the solution, thus simplifying the computation of multicomponent equilibria.

The computation of geochemical equilibria using MINTEQ involves distributing the total mass of each component among the various solid phases, surface sites, and aqueous ion-complexes. The distribution of components is calculated using equilibrium thermodynamic relationships. A typical reaction is

$$\nu_{xz}\, x + \nu_{yz}\, y \rightleftarrows z \tag{3.2}$$

where x and y are components in the aqueous phase and z is either an aqueous-phase ion-complex or a solid phase, and ν_{xz} and ν_{yz} are stoichiometric coefficients for components x and y of phase z, respectively. The reaction has the corresponding equilibrium relationship

$$a_z = K_z \prod_j (m_j\, \gamma_j)^{\nu_{zj}} \tag{3.3}$$

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where a_z and K_z are the activity and equilibrium constant, respectively, for formation of species, z; m_j and γ_j are the molality and activity coefficient, respectively, of component, j; and ν_{zj} is the stoichiometric coefficient for the jth component in species, z. The product (symbolized by π) is taken over all components. The thermodynamic activity of a component is based on the difference in chemical potential between the component in solution and the component in its standard state. (In MINTEQ calculations, the standard state is an infinitely dilute solution of the component in water.) Thermodynamic activity is a measure of the chemical driving force of a particular component in a reaction. For each component, the thermodynamic activity is related to the concentration by an activity coefficient. In MINTEQ, the activity coefficients (γ_i) are calculated for solute components using either the Davies equation or the extended Debye-Hückel equation, and the activity of water is calculated using an approximation to Raoult's law. Activity coefficients for neutral species are computed by

$$\log \gamma_i = 0.1I \qquad (3.4)$$

where I is the ionic strength.

An additional correction to the thermodynamic activity of a component is the distribution of the component among the aqueous ion-complexes. The distribution is made according to equilibrium relationships, such as the example given above. This calculation forms the speciation portion of MINTEQ. The ion-complexes are called Type 2 species in the MINTEQ model.

Adsorption is treated similarly to ion-complexation during the aqueous-speciation calculation. Each sorption reaction has a mass action equation similar to the speciation reactions, and the surface-bound ions are included in the mass balance totals for each component. In addition, the surface site must be introduced as a component with a mass balance equation for all of the surface species included. Finally, equations for the surface electrostatic potential are introduced that are analogous to activity corrections for aqueous ion-complexes.

The components are distributed into each solid phase in the equilibrium assemblage. Following the speciation calculations, the activity of each potential solid is calculated using the equilibrium expression given in Equation (3.3). If the saturation index of that solid is less than zero, the solid is not stable (i.e., is undersaturated). If the saturation index of the solid is greater than or equal to zero, the potential solid is considered to be saturated and is entered into the equilibrium assemblage. The speciation calculation is solved again with the addition of the solid phase to the calculations, thus decreasing the number of degrees of freedom by one. Solids included in the equilibrium assemblage and potential solids are called Type 4 and Type 5 species, respectively. (Refer to Chapter 9 for more detail on the various species types in the MINTEQ computer code.)

The thermodynamic data in the MINTEQ data base consist of the value of the equilibrium constant at 25°C, as well as the temperature dependence of the equilibrium constant for each reaction. In general, the temperature dependence for such an equilibrium constant is obtained through integration of the heat capacity difference function from 25°C to the temperature of interest. For certain reactions in the MINTEQ data base, an analytic expression based on such an integration is available. For other reactions, the heat capacity difference is assumed to be constant, and the Van't Hoff equation is used to provide the temperature dependence of the equilibrium constant. For a few reactions in the data base where no other thermodynamic data are available, the equilibrium constants are assumed to be temperature independent.

Each component is associated with a mass balance expression; the total mass of that component forms one degree of freedom for the system. The distribution of the component masses into the ion-complexes, surface sites, and solid phases is constrained by the total mass of each component. Because of the nature of aqueous solutions, three components are treated somewhat differently from the rest of the components.

The first of these components is water. Because the number of moles of water in the system is at least 10^4 times larger than typical amounts of the major dissolved constituents, the mass of water is considered a constant for the system. Water released from the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$), for example, is neglected. Thus, no mass balance equation is used for water, although it appears as a component in reactions that produce ion-complexes and solids.

The second component is hydrogen. Analytically, hydrogen is measured in terms of an activity (i.e., pH) rather than in terms of mass. As a component, hydrogen can be treated like water with the activity fixed at a given pH and the mass balance ignored. This method requires that the equilibrium pH is known. Alternatively, a total mass of ionizable hydrogen can be computed using charge balance and using the mass total for hydrogen.

The third component that is treated differently in MINTEQ is the electron. Table 9.1 (Chapter 9) shows that each redox-sensitive element appears as a separate component for each valance state. The electron activity is used to represent the relationship between the different valance states of the same element. Because negligible quantities of free electrons actually exist in solution, no mass balance equation is used for the electron. The electron activity can be fixed for a particular system if the equilibrium pe (negative log of electron activity) is known. In this case, the redox reactions are declared Type 3 and fix the ratios of the activities of the various redox couples (e.g., Fe^{2+}/Fe^{3+}). If the equilibrium pe is to be calculated, the electron is not used as a component at all, and the pe is computed from the activity ratios of the components of each redox couple.

CHAPTER 4

TYPES OF GEOCHEMISTRY COMPUTER CODES

Several types of solution algorithms are incorporated into geochemical computer codes. Thus, given a problem defined by geochemical equilibria, many different techniques can be used to calculate numerical solutions. In this chapter, these computational approaches are discussed with the goal of placing the approach used in the MINTEQ code in proper context.

As discussed in the previous chapter, the general problem of geochemical equilibria is determining the solution of a set of mass balance equations, one for each component. Because the mass action constraints are nonlinear in the components, the problem reduces to the solution of a system of nonlinear equations. (The problem can also be viewed as the minimization of free energy of the system under the mass balance constraints. Van Zeggeren and Storey (1970) showed that these two conceptualizations are mathematically equivalent.)

Back substitution methods, such as the ligand projection method used in EQUILIB and successive iteration methods (using Jacobi or Gauss-Seidel iteration), converge well from poor initial activity guesses. These methods converge relatively slowly (first order) near the solution, however. The Newton-Raphson method converges rapidly (second order) near the solution but may not converge from poor initial activity guesses. Because it is more efficient than the substitution methods, the Newton-Raphson algorithm was incorporated in a number of geochemical codes, including PHREEQE (Parkhurst et al. 1980), EQ3NR (Wolery 1983), and MINTEQ (Felmy et al. 1984b).

Another difference in the computer codes arises from the treatment of solubility equilibria. In the MINTEQ code, when a solid enters the equilibrium assemblage, the system of mass balance equations is modified to incorporate the additional solubility constraint (This modification is discussed in detail in Chapter 7). The system is then solved directly using the Newton-Raphson technique.

The PHREEQE and EQ3/6 codes have the capability to follow a reaction path during mass transfer calculations. When a solid becomes oversaturated and enters the equilibrium assemblage, the equilibration is done in a series of steps forming a reaction path. The reaction path treatment is slower and more complicated than the direct treatment but does provide a limited capability to model kinetically controlled reactions.

CHAPTER 5

ASSUMPTIONS AND LIMITATIONS

The geochemical modeling assumptions and limitations imposed by the MINTEQ computer code are explained in detail in Felmy et al. (1984b). For convenience, some of the assumptions and limitations will be briefly mentioned here. The assumptions inherent in MINTEQ take two forms: 1) assumptions that come from the chemical theories incorporated into MINTEQ and 2) assumptions dictated by the thermodynamic data in the MINTEQ data base, and the modification of those thermodynamic data to other conditions.

The key assumption in the MINTEQ computer code is that the system is at equilibrium. MINTEQ will not explicitly consider kinetics. There is no coding structure in MINTEQ that would allow one to enter kinetic data. However, this is not a major limitation of the code because of the paucity of available kinetic data. Kinetics may be partially addressed by the user only in the sense that the user may select the equilibrium solid-phase assemblage.

An example of an assumption that comes from the chemical theories used in MINTEQ is the ion association theory. The MINTEQ computer code employs the ion association theory to compute aqueous speciation while other ion interaction theories, such as those of Harvie and Weare (1980), may be more applicable to certain waste solutions.

Perhaps the most important assumptions imposed by the use of any computer code come from the thermodynamic data and the modification of the thermodynamic data. For instance, when using MINTEQ or any computer code to determine the speciation of the constituents of a given water sample, the user is assuming 1) the thermodynamic data for the species considered are complete (i.e., there are no missing data that are important) and 2) the thermodynamic data in the code are accurate. As will be explained in Chapter 8, the thermodynamic data file in the MINTEQ code was developed over a period of years. Different versions of these thermodynamic data are available and upgrades to the data have been provided by several researchers. The user of a computer code assumes responsibility for ensuring that the thermodynamic data in the code used are complete and accurate with regards to the system modeled.

Other assumptions involve the modification of the thermodynamic data to fit other conditions. The equilibrium constants in the MINTEQ data base are given for 25°C. If the water data entered into the input file are at a different temperature, MINTEQ uses either the Van't Hoff equation or analytical expressions for the log K as a function of temperature to correct the log Ks for temperature. Where available, the analytical expressions of log K, as a function of temperature, are used. When analytical expressions are not available, MINTEQ will use the Van't Hoff equation to compute the log K at another temperature. The Van't Hoff equation assumes that the enthalpy values entered in MINTEQ are independent of temperature, which may not be true. Because of these limitations, MINTEQ should not be used to model solutions at temperatures greater than 100C. For many of the data in the MINTEQ data base, neither analytical expressions nor enthalpies are available. In these cases, MINTEQ will use the log Ks at 25C for modeling the speciation at all other temperatures. Again, it is the responsibility of the user to determine that the equilibrium constants can be accurately modified to the desired temperature or ensure that any temperature modifications are applicable.

The MINTEQ code uses either the extended Debye-Hückel or Davies equation to compute the activity coefficients for particular ions. The activity coefficients are used to modify the log Ks to ionic strengths other than zero. The extended Debye-Hückel equation is

$$\log_{10} \gamma_i = \frac{-A_d Z_i^2 \sqrt{I}}{1 + B_d a_i \sqrt{I}} + b_i I \tag{5.1}$$

where A_d and B_d are the Debye-Hückel constants that depend on the dielectric constant and temperature

γ_i = activity coefficient of i^{th} species

Z_i = charge on species i

a_i = ion size parameter

b_i = ion specific parameter which allows for the decrease in solvent concentration in concentrated solutions (Truesdell and Jones 1974)

I = ionic strength

The A_d and B_d constants are computed as described in Truesdell and Jones (1974). The a_i and b_i parameters used in the MINTEQ data base were taken directly from the WATEQ3 data base (Ball et al. 1981). The Davies equation

$$\log \gamma_i = -A\, Z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3\, I\right) \tag{5.2}$$

requires fewer parameters. If the parameters for a_i and b_i are available, MINTEQ will use the extended Debye-Hückel equation to compute activity coefficients. If these parameters are not in the MINTEQ data base, MINTEQ will default to the Davies equation. Neither of the activity coefficient correction methods should be used above an ionic strength of 0.5 molal. MINTEQ also has a "user-defined" option that mandates the use of the Davies equation.

MINTEQ has no capability to consider solid solutions. That is, it is impossible to automatically vary the composition of a precipitating solid as the solution composition changes.

CHAPTER 6

DATA REQUIREMENTS

In the MINTEQ geochemical code, the data required to define a geochemical problem have been divided into two types. Details on these data are provided in Chapter 9. Only an overview of the types of data will be given here. The first type of data is specific to each geochemical problem and consists of information needed to define chemical conditions for a particular system. The second type of data resides in the thermodynamic data base; subsets of this data are used to solve all geochemical equilibria. The division into problem-specific data and thermodynamic data was made to minimize the amount of data entered by an operator to solve a single problem. In addition, use of a standard thermodynamic data base facilitates comparison of MINTEQ results from user to user.

The problem-specific data consist of the information needed to specify the geochemical system under consideration. The composition, temperature, and pressure must be input in order to define the model system. The first portion of the input file is designed to identify the components and their analytic totals. An activity guess can also be specified for each component as a convergence aid. (If no activity guess is input, MINTEQ will construct an activity guess by dividing the analytic total by 10.) The second portion of the input file is a listing of the solids to be considered in the problem, solids that actually are in the problem, relationships that act as activity constraints, and any monitored species (the concentration of a monitored species is output for informational purposes but does not enter into the problem).

The thermodynamic data base contains equilibrium constants and stoichiometries for the reactions involving the aqueous complexes, redox couples, and solid phases. When available, the temperature dependence of the equilibrium constants is also given. After the component list is input, MINTEQ searches the thermodynamic data base for the aqueous ion-complexes that can be formed from the components. After the type modifications are entered, the thermodynamic constants for each of the solid phases and activity constraints are obtained from the data base. If a reaction is not in the thermodynamic data base, the stoichiometry and equilibrium constants can be entered in the user input data.

One exception to this general scheme is the treatment of sorption reactions. Because several different sorption mechanisms can be modeled using MINTEQ, no thermodynamic data for sorption reactions are included in the thermodynamic data base. All of the data necessary to model sorption reactions must be input by the user.

CHAPTER 7

METHODOLOGY FOR SOLVING CHEMICAL EQUILIBRIUM PROBLEMS

The path that MINTEQ uses to solve a chemical equilibrium problem is shown in Figure 7.1. We will step through the solution of a typical problem to give the user a feel for what the code does with the input data. The data handling performed by the MINTEQ computer code will be discussed but only to the extent necessary to display the workings of the code.

Remember that the code is solving a mass balance problem using mass action relationships. Consider, for example, the problem of determining the equilibrium composition of a solution to which 10^{-3} moles/liter of $CaCO_3$ were added. (Westall et al. (1976) present this in the MINEQL documentation.) For this system, the components are Ca^{2+}, H^+, CO_3^{2-}, and H_2O. The choice of components is arbitrary. Morel (1983) has a good discussion on the concept of components and their selection for this type of application. The only stipulation on the choice of components is that the components chosen must provide a unique stoichiometric formula for each chemical species in the system. That is, all the species that you consider important to the system must be capable of being uniquely formed from a linear combination of these components. The matrix for this system is shown in Table 7.1. The column headings represent the components, and the row headings represent the species derived from the components. The numbers in the columns and rows represent the mass balance and mass action stoichiometries, respectively. From mass balance constraints (ignoring the gas phase) the following relationships are true for this example:

$$C_{T,Ca^{2+}} = C_{Ca^{2+}} + C_{CaCO_3^o} + C_{CaHCO_3^+} + C_{CaOH^+}$$

$$C_{T,H^+} = C_{H^+} + C_{CaHCO_3^+} + C_{HCO_3^-} + 2C_{H_2CO_3} - C_{OH^-} - C_{CaOH^-}$$

$$C_{T,CO_3^{2-}} = C_{CO_3^{2-}} + C_{CaCO_3^o} + C_{CaHCO_3^+} + C_{H_2CO_3} + C_{HCO_3^-}$$

$$C_{T,H_2O} = C_{H_2O} + C_{OH^-} + C_{CaOH^+}$$

where C_T is the input analytical molality of the component expressed in the form the component takes in the MINTEQ data base, and C is the concentration in molality of the ions and complexes.

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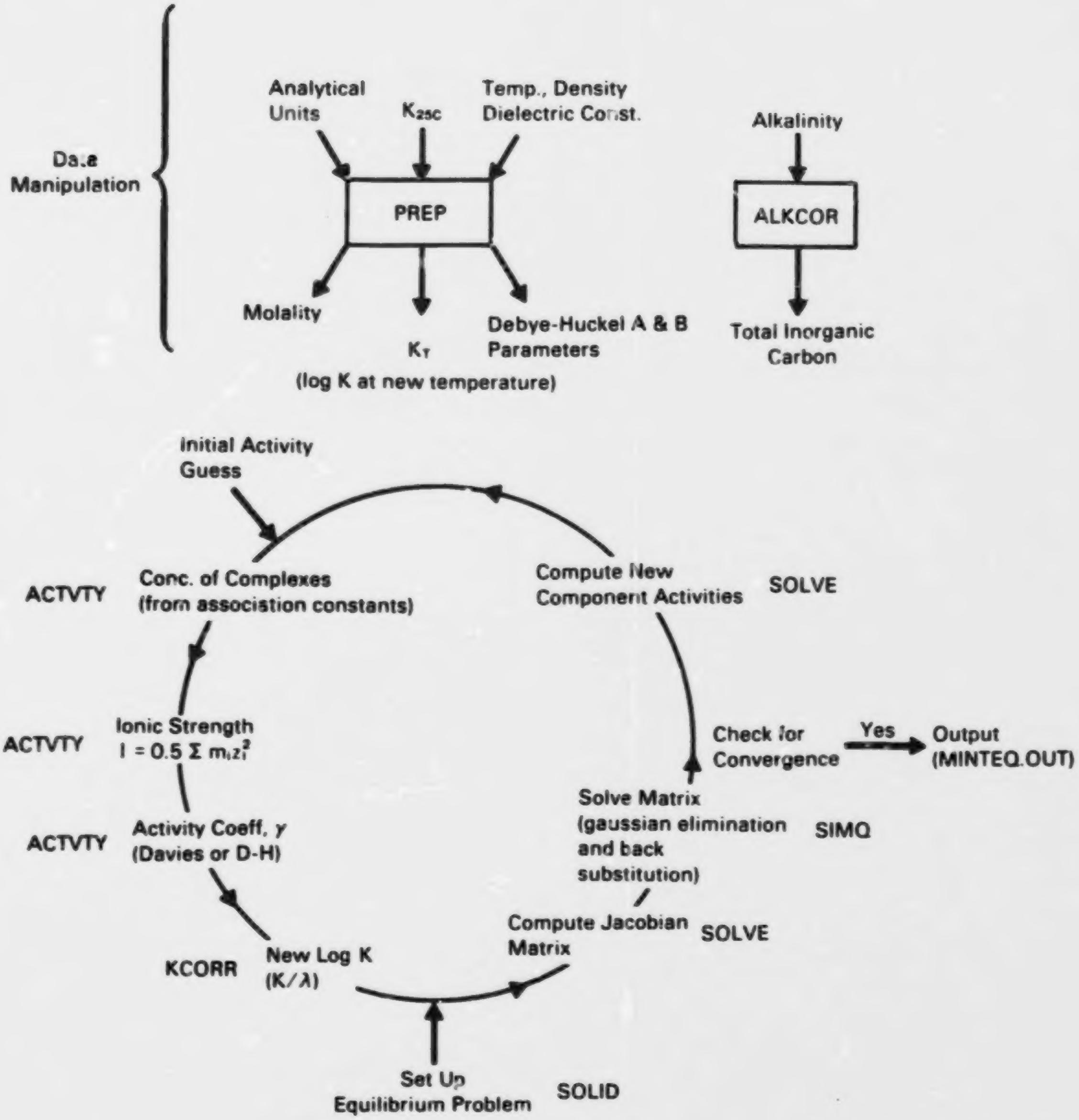
Data Manipulation
Analytical Units
K25C
Temp., Density Dielectric Const.
PREP
Molality
KT
(log K at new temperature)
Debye-Huckel A & B Parameters
Alkalinity
ALKCOR
Total Inorganic Carbon
Initial Activity Guess
ACTVTY
Conc. of Complexes (from association constants)
Compute New Component Activities
SOLVE
ACTVTY
Ionic Strength I = 0.5 Σ mizi2
Check for Convergence
Yes
Output (MINTEQ.OUT)
ACTVTY
Activity Coeff. γ (Davies or D-H)
Solve Matrix (gaussian elimination and back substitution)
SIMQ
KCORR
New Log K (K/λ)
Compute Jacobian Matrix
SOLVE
Set Up Equilibrium Problem
SOLID

FIGURE 7.1. Path that MINTEQ Uses in Solving a Chemical Equilibrium Problem

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TABLE 7.1. Formation of Species from Components

	Ca^{2+}	$\mathrm{CO}_3{}^{2-}$	H^+	$\mathrm{H}_2\mathrm{O}$
Ca^{2+}	1	0	0	0
$\mathrm{CaCO}_3{}^{o}$	1	1	0	0
$\mathrm{CaHCO}_3{}^{+}$	1	1	1	0
CaOH^+	1	0	-1	1
$\mathrm{CO}_3{}^{2-}$	0	1	0	0
$\mathrm{HCO}_3{}^{-}$	0	1	1	0
$\mathrm{H}_2\mathrm{CO}_3$	0	1	2	0
OH^-	0	0	-1	1
$\mathrm{H}_2\mathrm{O}$	0	0	0	1
H^+	0	0	1	0

These equations are rearranged into a set from which a guess at some of the values (the activities of the components) can be made and from which the concentrations of the complexes can be calculated. The total concentration of each component is calculated by summing the concentrations of the components in the individual species that contain the component. The sum of the calculated concentrations can then be compared to the known analytical concentration of the component to determine the accuracy of the initial guesses. MINTEQ uses the mass action expressions to modify the mass balance equations into the form necessary for the calculations. The concentrations of the complexes are calculated in the following expressions:

$$C_{\mathrm{Ca}^{2+}} = \frac{a_{\mathrm{Ca}^{2+}}}{\gamma_{\mathrm{Ca}^{2+}}}$$

$$\mathrm{Ca}^{2+} + \mathrm{CO}_3^{2-} \rightleftarrows \mathrm{CaCO}_3^{o} \; ; \; K^{a}_{\mathrm{CaCO}_3^{o}} = \frac{a_{\mathrm{CaCO}_3^{o}}}{a_{\mathrm{Ca}^{2+}} \; a_{\mathrm{CO}_3^{2-}}} \; ;$$

$$C_{\mathrm{CaCO}_3^{o}} = \frac{K^{a}_{\mathrm{CaCO}_3^{o}}}{\gamma_{\mathrm{CaCO}_3^{o}}} \, a_{\mathrm{Ca}^{2+}} \cdot a_{\mathrm{CO}_3^{2-}}$$

$$Ca^{2+} + H^+ + CO_3^{2-} \rightleftarrows CaHCO_3^+ \; ; \; K^a_{CaHCO_3^+} = \frac{a_{CaHCO_3^+}}{a_{Ca^{2+}} \, a_{H^+} \, a_{CO_3^{2-}}} \; ;$$

$$C_{CaHCO_3^+} = \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}} \, a_{Ca^{2+}} \, a_{H^+} \, a_{CO_3^{2-}}$$

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ ; \; K^a_{CaOH^+} = \frac{a_{CaOH^+} \, a_{H^+}}{a_{Ca^{2+}} \, a_{H_2O}} \; ;$$

$$C_{CaOH^+} = \frac{K^a_{CaOH^+}}{\gamma_{CaOH^+}} \, \frac{a_{Ca^{2+}} \, a_{H_2O}}{a_{H^+}}$$

$$C_{H^+} = \frac{a_{H^+}}{\gamma_{H^+}}$$

$$H^+ + CO_3^{2-} = HCO_3^- \; ; \; K^a_{HCO_3^-} = \frac{a_{HCO_3^-}}{a_{H^+} \, a_{CO_3^{2-}}} \; ; \; C_{HCO_3^-} = \frac{K^a_{HCO_3^-}}{\gamma_{HCO_3^-}} \, a_{H^+} \, a_{CO_3^{2-}}$$

$$2H^+ + CO_3^{2-} = H_2CO_3^* \; ; \; K^a_{H_2CO_3^*} = \frac{a_{H_2CO_3^*}}{a_H^2 \; a_{CO_3^{2-}}} \; ;$$

$$C_{H_2CO_3^*} = \frac{K^a_{H_2CO_3^*}}{\gamma_{H_2CO_3^*}} \, a^2_{H^+} \, a_{CO_3^{2-}}$$

$$H_2O \rightleftarrows OH^- + H^+ \; ; \; K^a_{OH} = \frac{a_{OH^-} \, a_{H^+}}{a_{H_2O}} \; ; \; C_{OH^-} = \frac{K^a_{OH^-}}{\gamma_{OH^-}} \, \frac{a_{H_2O}}{a_{H^+}}$$

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$$C_{CO_3^{2-}} = \frac{a_{CO_3^{2-}}}{\gamma_{CO_3^{2-}}}$$

where K^a = association constant for the reaction
a = activity of the species
γ = activity coefficient of the species
$^*H_2CO_3$ = dissolved CO_2 is treated as H_2CO_3

Once an expression exists to calculate the concentration of each of the complexes of interest; the appropriate expressions (terms) can be summed to give the following total analytical molalities of the desired components:

$$C_T,Ca^{2+} = \frac{a_{Ca^{2+}}}{\gamma_{Ca^{2+}}} + \frac{K^a_{CaCO_3^o}}{\gamma_{CaCO_3^o}} a_{Ca^{2+}} a_{CO_3^{2-}}$$

$$+ \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}} a_{Ca^{2+}} a_{H^+} a_{CO_3^{2-}} + \frac{K^a_{CaOH^+}}{\gamma_{CaOH^+}} \frac{a_{Ca^{2+}} a_{H_2O}}{a_{H^+}}$$

$$C_T,H^+ = \frac{a_{H^+}}{\gamma_{H^+}} + \frac{K^a_{CaHCO_3^+}}{CaHCO_3^+} a_{Ca^{2+}} a_{H^+} a_{CO_3^{2-}}$$

$$+ \frac{K^a_{HCO_3^-}}{\gamma_{HCO_3^-}} a_{H^+} a_{CO_3^{2-}} + 2 \frac{K^a_{H_2CO_3^*}}{\gamma_{H_2CO_3^*}} a^2_{H^+} a_{CO_3^{2-}}$$

$$- \frac{K^a_{OH^-}}{\gamma_{OH^-}} \frac{a_{H_2O}}{a_{H^+}} - \frac{K^a_{CaOH^-}}{\gamma_{CaOH^-}} \frac{a_{H_2O}}{a_{H^+}} a_{Ca^{2+}}$$

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$$C_{T,CO_3^{2-}} = \frac{a_{CO_3^{2-}}}{\gamma_{CO_3^{2-}}} + \frac{K^a_{CaCO_3^o}}{\gamma_{CaCO_3^o}} a_{Ca^{2+}} a_{CO_3^{2-}}$$

$$+ \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}} a_{Ca^{2+}} a_{H^+} a_{CO_3^{2-}} + \frac{K^a_{H_2CO_3^*}}{\gamma_{H_2CO_3^*}} a^2_{H^+} a_{CO_3^{2-}}$$

$$+ \frac{K^a_{HCO_3^-}}{\gamma_{HCO_3^-}} a_{H^+} a_{CO_3^{2-}}$$

$$C_{T,H_2O} = \frac{a_{H_2O}}{\gamma_{H_2O}} + \frac{K^a_{CaOH^+}}{\gamma_{CaOH^+}} \frac{a_{Ca^{2+}} a_{H_2O}}{a_{H^+}} + \frac{K^a_{OH^-}}{\gamma_{OH^-}} \frac{a_{H_2O}}{a_{H^+}}$$

Note that these equations are now all in terms of either constants (K^a), activity coefficients (gammas, γ_i, which are calculated from the ionic strength) or the activities of the components (a_i) for which guesses can be made; these are the equations that are solved by MINTEQ. There will be one equation for each component and one term in each equation for each complex that contains that component. The analytical mass totals of each component are supplied by the modeler as input. Thus, only the activities are unknowns, and they are determined as follows.

Subroutine PREP (Figure 7.1) performs the important functions of

- converting whatever analytical units are provided (mol, mg/L, ppm) to molal units.
- calculating the log K at the solution temperature using either a power function with empirical constants or the Van't Hoff equation in conjunction with the enthalpy value depending on the data provided (if the requisite data are missing so that neither of these methods for calculating the log K at the new temperature is possible, then the log K at 25 C is used).
- calculating the Debye-Hückel (D-H) A and B parameters using data on solution temperature, density, and the dielectric constant of the solution. [Note: these are not the ion size parameters (A and B) in the extended D-H equation. The ion size parameters are input data from the Analyt.dat file].

Subroutine ALKCOR takes the alkalinity data if it is input (Option 1 = 1) and converts it to total inorganic carbon.

We are now ready to enter the loop that will solve the chemical equilibrium problem. The primary goal of subroutine ACTVTY is to determine activity coefficients to use in the mass balance equations. The activity coefficients are a function of the ionic strength of the solution that is calculated from the concentrations of the charged species in solution. The distribution of charged species is affected by the activities of the ions (components) so ACTVTY starts at the activity guesses to generate reasonable activity coefficients. Subroutine ACTVTY takes either the initial activity guesses for the components given in the input data file or computes its own guess by dividing the analytical molality by 100 to obtain a starting point for the computations. The concentrations of the complexes can be calculated from these activity guesses by using the association constants. These concentrations probably won't be correct but they will be better than using the concentrations of the components to make the initial ionic strength calculation. Then, using either the Davies or extended Debye-Huckel equation, ACTVTY calculates an activity coefficient for all aqueous species. Subroutine KCORR takes these activity coefficients and computes a new log K for each species by dividing and/or multiplying the original log K by the appropriate activity coefficients. Mass balance expressions are modified by substituting in the new log K values and then solved again.

The aqueous problem is now fully specified. If a solid, such as calcite, is imposed on the system, then the mass balance equations are altered (by subroutine SOLID); this takes into account that one of the components can now be dropped from the mass balance equations because it is specified by the solid. For example, if calcite is imposed, then the mass balance equations are altered by substituting a mass action constraint for the activity of the carbonate component, and the carbonate species can then be dropped from the list of components. The mass action expressions for the calcite solid, written in terms of the carbonate species, can be substituted into the mass balance expressions as follows:

$$Ca^{2+} + CO_3^{2-} = CaCO_{3(s)} \; ; \; K_{sp\ calcite} = \frac{1}{a_{Ca^{2+}}\, a_{CO_3^{2-}}}$$

$$a_{CO_3^{2-}} = \frac{1}{K_{sp\ calcite}\, a_{Ca^{2+}}}$$

The final equations to solve for the system are now

$$C_{T,Ca^{2+}} = \frac{a_{Ca^{2+}}}{\gamma_{Ca^{2+}}} + \frac{K^a_{CaCO_3^0}}{\gamma_{CaCO_3^0}\, K_{sp\ calcite}} + \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}}\, \frac{a_{H^+}}{K^a_{sp\ calcite}}$$

$$+ \frac{K^a_{CaOH^+}}{\gamma_{CaOH^+}}\, \frac{a_{Ca^{2+}}\, a_{H_2O}}{a_{H^+}}$$

$$C_{T,H^+} = \frac{a_{H^+}}{\gamma_{H^+}} + \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}}\, \frac{a_{H^+}}{K_{sp\ calcite}} + \frac{K^a_{HCO_3^-}}{\gamma_{HCO_3^-}}\, \frac{a_{H^+}}{K_{sp\ calcite}\, a_{Ca^{2+}}}$$

$$+ 2\, \frac{K^a_{H_2CO_3^*}}{\gamma_{H_2CO_3^*}}\, \frac{a^2_{H^+}}{K_{sp\ calcite}\, a_{Ca^{2+}}} - \frac{K^a_{OH^-}}{\gamma_{OH^-}}\, \frac{a_{H_2O}}{a_{H^+}} - \frac{K^a_{CaOH^-}\, a_{H_2O}\, a_{Ca^{2+}}}{\gamma_{CaOH^-}\, a_{H^+}}$$

$$C_{T,CO_3^{2-}} = \frac{1}{\gamma_{CO_3^{2-}}\, K_{sp\ calcite}\, a_{Ca^{2+}}} + \frac{K^a_{CaCO_3^0}}{\gamma_{CaCO_3^0}\, K_{sp\ calcite}} + \frac{K^a_{CaHCO_3^+}}{\gamma_{CaHCO_3^+}}\, \frac{a_{H^+}}{K_{sp\ calcite}}$$

$$+ \frac{K^a_{H_2CO_3^*}\, a^2_{H^+}}{\gamma_{H_2CO_3^*}\, K_{sp\ calcite}\, a_{Ca^{2+}}} + \frac{K^a_{HCO_3^-}\, a_{H^+}}{\gamma_{HCO_3^-}\, K_{sp\ calcite}\, a_{Ca^{2+}}}$$

$$C_{T,H_2O} = \frac{a_{H_2O}}{\gamma_{H_2O}} + \frac{K^a_{CaOH^+}}{\gamma_{CaOH^+}}\, \frac{a_{Ca^{2+}}\, a_{H_2O}}{a_{H^+}} + \frac{K^a_{OH^-}\, a_{H_2O}}{\gamma_{OH^-}\, a_{H^+}}$$

Again, the resulting set of equations are basically the same as those equations solved without the solid except that carbonate was dropped as a component, and mass action expressions for calcite were included.

The set of equations are solved using subroutine SOLVE and the Newton-Raphson iteration method. In this method, the difference in component concentration between the result of the computation using the last guess at the component activity and the actual analytical concentration (the difference function) is used with the partial derivative of the difference functions to make a new guess at the component activities. The Jacobian matrix computed by SOLVE is simply the matrix of the partial derivatives. The matrix is solved by SIMQ, and a new mass total for each component is calculated. This new mass total is compared to the analytical mass total to determine if the difference is within the tolerance limit that the computer code specifies. If the difference is within the tolerance criterion, the problem is considered solved. If the difference is not within the tolerance criterion, then the new activities calculated by the Newton-Raphson method are used to start the loop over again. Adsorption equations are incorporated into the mass balance equations and the new equations are solved analogously to those equations employed for aqueous complexation.

CHAPTER 8

MODELING APPROACH

GEOCHEMICAL COMPUTER CODE

Before beginning to create MINTEQ input files for modeling (Chapter 9), we will briefly discuss the structure of MINTEQ. Additionally, some of the features of MINTEQ will be compared to other codes. Finally, we will discuss the methodology involved in developing the conceptual chemical model of the system that is used in conjunction with the computer code.

The MINTEQ (Felmy et al. 1984b) geochemical computer code can be used to perform the calculations necessary to simulate (model) the contact of aqueous solutions with solid phase assemblages or to perform simple ion speciation/solubility calculations. MINTEQ integrates many of the capabilities of its two immediate predecessors, WATEQ3 (Ball et al. 1981) and MINEQL (Westall et al. 1976), that are advantageous in modeling studies. MINTEQ can calculate ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. Moreover, MINTEQ has the capability to accept a finite mass for any solid considered for dissolution. Therefore, MINTEQ will dissolve the specified solid phase only until its initial mass is exhausted. MINTEQ is the only member of the REDEQL family of computer codes known to have this capability. Members of this family of computer codes include REDEQL (Morel and Morgan 1972), REDEQL2 (McDuff and Morel 1973), GEOCHEM (Sposito and Mattigod 1980), and MINEQL (Westall et al. 1976).

The ability to accept a finite mass enables MINTEQ to model flow-through systems. In these systems, the masses of solid phases that precipitated at earlier pore volumes can be dissolved at later pore volumes according to thermodynamic constraints imposed by the solution composition and solid phases present. For a discussion of other geochemical computer codes, the reader is referred to Jenne (1981). Kincaid et al. (1984a,b), after an exhaustive study of the extant geochemical computer codes, recommended MINTEQ (Felmy et al. 1984b) and EQ3/EQ6 (Wolery 1979, 1983) as the best available codes for modeling solute migration.

The completeness and credibility of the code's thermodynamic data base are important factors in the selection of a geochemical code. The thermodynamic data base in MINTEQ was taken from the data base of WATEQ3 and is thus well documented. The WATEQ3 data base was developed and documented over a period of years by members of the United States Geological Survey (USGS) (Truesdell and Jones 1974; Ball et al. 1980, 1981). The MINTEQ data base (Felmy et al. 1984b) has been expanded using published critical reviews and studies of the aqueous species and solids of Cr, Cu(II), Pu, Tc, and U (Schmidt 1984; Rard 1983; Cowan

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1984; Lemire and Tremaine 1983). In addition, preliminary compilations have been completed by S. R. Peterson, W. J. Deutsch, and K. M. Krupka at PNL for the aqueous species and solids of Co, Mo, Ra, Se, Th, Hg, Sb, Ce, Cs, Tl, and V. The thermodynamic data selected in the compilations are primarily based on accepted tabulations found in sources, such as the U.S. National Bureau of Standards (Wagman et al. 1982), the committee on Data from Science and Technology of the International Council of Scientific Unions (CODATA Task Group 1977), and the USGS (Robie et al. 1978).

The thermodynamic data base for a code should be as complete as possible. All components in the MINTEQ thermodynamic data base are potentially important in modeling contaminant migration even though that component (element or species) may not be a constituent of the initial waste solution. The waste solution may react with surrounding sediments or indigenous migrating solutions that do contain the specified component. The components that exist in the soil environment and are not associated with the waste solution could then be important in the complexation reactions, precipitation/dissolution reactions, or redox reactions that affect the concentrations of components found in the unreacted waste solution.

Other factors are important in the selection of a geochemical computer code. Unlike certain codes [PHREEQE (Parkhurst et al. 1980)], MINTEQ has the ability to automatically select and equilibrate a solution, using those solids listed in the data base most thermodynamically stable in response to changes in solution composition. PHREEQE, on the other hand, will not automatically consider all solids in the data base that could enter into the equilibrium calculations. The MINTEQ computer program can also recompute the pH and pe (negative log of electron activity) as the solution composition changes in response to aqueous speciation, precipitation, and dissolution of solid phases. The pH is computed from a modified form of the electroneutrality condition, commonly termed the proton condition (Morel and Morgan 1972). The pe is calculated by initializing the mass totals for each oxidation state of an element and including a redox reaction between the components of each oxidation state. Alternatively, the pH and pe can be fixed at the analytically measured values. Further details on the computational methods are provided in Felmy et al. (1984b) and Westall et al. (1976) and in various sections of this document. The MINTEQ computer code can also model adsorption reactions and is "user friendly". Adsorption reactions are important in many natural systems, and MINTEQ has several adsorption algorithms available for use.

The MINTEQ computer code can be considered to have four parts: 1) a speciation submodel, 2) a solubility submodel, 3) a mass transfer submodel and 4) an adsorption submodel. The calculations completed by each submodel are dependent on the thermodynamic data stored in the MINTEQ data base. Because of their interrelationship, the ion speciation and solubility submodels will be discussed together.

ION SPECIATION/SOLUBILITY CALCULATIONS

In the speciation submodel, MINTEQ computes the activities of complexed and uncomplexed cationic and anionic species, neutral ion pairs, and the activities of cationic and anionic redox species. These activities are then fed to the solubility submodel. The solubility submodel performs solubility calculations in which ion activity products for solids and minerals are calculated. The calculated activity products (CAP) are compared to the solubility products (K) of minerals and solids, stored in the thermodynamic data base of MINTEQ, to develop a saturation or disequilibrium index [log (AP/K)]. This saturation index indicates the degree of undersaturation or oversaturation of a solution, relative to solids and minerals of interest. If a solution is oversaturated with respect to a particular solid phase, the value of the saturation index is greater than zero [log (AP/K)>0]. The existence of oversaturated conditions is usually explained by precipitation kinetics and/or mineralogical factors that prevent the solid from precipitating at a rate sufficient to control the concentrations of its dissolved components. If the saturation index reflects undersaturation [log(AP/K)<0], it is concluded that either 1) a less soluble (more thermodynamically stable) solid is controlling the dissolved constituents' concentrations, 2) another mechanism, such as adsorption, is controlling the concentrations of the component species below their solubility products or 3) the constituents' concentrations in the source are low (i.e., undersaturated with respect to considered solid phase controls). The activity coefficient corrections used in calculating the activity products are based on either the extended Debye-Hückel equation with two adjustable parameters (Truesdell and Jones 1974) or, alternatively, the Davies equation (Davies 1962).

MASS TRANSFER CALCULATIONS

The results from the solubility submodel of MINTEQ are used by the mass transfer submodel to calculate the mass of solid that "precipitates" or "dissolves". MINTEQ keeps track of the mass of solid that precipitates from solution or dissolves from the sediment. These solids are used to represent the heterogeneous sediment and the solution. The solids that represent the solution are those considered likely to precipitate from solution because of changes that occur in specific solution parameters (e.g., pH and pe) on contact of the solution with the assemblage of solid phases (chemical model) used to represent the sediment. If the solubility submodel indicates that a given solution is oversaturated, with respect to a solid phase considered in the conceptual model of the system, the mass transfer submodel will "precipitate" that solid phase until the solution is at equilibrium [i.e., log (AP/K) = 0] with the solid. If the solubility submodel computes a solution to be undersaturated, with regard to a particular solid phase in the chemical model of the system, the MINTEQ mass transfer submodel will "dissolve" that solid until solution equilibrium is achieved, with respect to the solid, or until the user-specified finite mass of solid is completely dissolved.

MINTEQ is what might be termed a "single-step" or "single-point" geochemical computer code. Unlike EQ6 (Wolery 1979), MINTEQ was not constructed with the objective of performing reaction path calculations. Reaction path codes follow the path of irreversible reactions to a state of thermodynamic equilibrium. These codes can "titrate" a solution with small increments of specified solids until a state of thermodynamic equilibrium is achieved or until the solid or solids are exhausted. This titration amounts to computing a series of partial equilibria until the final equilibrium is reached. MINTEQ computes the final equilibrium of a given system in a "single-step". The details about the reaction path are, therefore, neglected. Through a difficult and convoluted process, MINTEQ could be constrained to perform reaction path calculations, but it is not recommended that it be used in this mode. A reaction path code would be useful if you were interested in not only knowing what solids precipitated or dissolved and their masses, but also if you were interested in knowing at what stage in the progress of a reaction these solids precipitated or dissolved and under what conditions. For most uses, it is sufficient to have a single-step code.

ADSORPTION CALCULATIONS

The MINTEQ computer code can model adsorption onto solid surfaces via several mechanisms: 1) an activity Kd, 2) an activity Langmuir isotherm, 3) an activity Freundlich isotherm, 4) an ion exchange model 5) a constant capacitance surface complexation model, and 6) a surface complexation triple-layer model (TLM). A general description of each algorithm can be found in Felmy et al. (1984b). Additional details on the mathematical formalism and nuances of the algorithms can be obtained from references cited in Felmy et al. (1984b).

CONCEPTUAL CHEMICAL MODEL DEVELOPMENT

A chemical model of a system may be developed through many different methods and thought processes. Plummer (1984) has conveniently classified the modeling approach into the "inverse" and "forward" methods. The inverse method, as described by Plummer, is similar to the inverse problem in hydrology (Freeze and Cherry 1979). The goal of both the inverse and forward methods is to identify the dominant mechanisms that account for concentration

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distributions of aqueous and solid phases along a flow path. These mechanisms involve such processes as precipitation/dissolution of solids, adsorption/desorption, ion exchange, and advection-dispersion. After the dominant mechanisms are identified and incorporated into a chemical model of the system, the chemical model can then be used in the forward mode to predict aqueous concentrations and mass transfer in yet unstudied systems.

The term "chemical evolution-path" designates the flow path along which mass transfer mechanisms (e.g., precipitation/dissolution, adsorption/desorption) operate. The inverse method of modeling is more quantitative than the forward method when appropriate hydrogeochemical data along the evolution-path are available. Using the inverse method, you work backward from observed data at two wells separated in space along a flow path. The objective is to find a reaction model that produces mass transfers along the flow path that are consistent with the data at the wells. The inverse method is not constrained by thermodynamics so the results should be checked by the forward method, which includes thermodynamic constraints on the plausible phases selected for the conceptual chemical model of the system. At the least, ion speciation/solubility calculations should be performed on the initial and final points (well data) in the system to check thermodynamic feasibility. In other words, the inverse method, beginning with the initial well data, produces mass transfers necessary to satisfy the well data at the final point unconstrained by thermodynamic considerations. A mass balance computer code, such as BALANCE (Parkhurst 1982), can use the inverse method to develop a model.

Instead of working backward from given data, the forward method uses a developed conceptual chemical model of the system to predict the aqueous compositions and mass transfers resulting from the sediment/solution interaction. A code, such as MINTEQ, has the capabilities to use a conceptual chemical model of the system to make predictions according to the forward method. This method is the only practical approach in the absence of analytical data sufficient to perform inverse modeling. This conceptual chemical model of the system may or may not be constrained by thermodynamic constraints. If unconstrained by thermodynamic data, the forward method differs from the inverse method only in that the forward method is used in a predictive mode. One may develop a chemical model by using the inverse method and subsequently using the chemical model in a forward mode to predict future water quality data and mass transfers or to predict water quality data and mass transfers for another site. If one tries to use thermodynamic constraints to make predictions regarding a site, the forward method is implied. These thermodynamic constraints are both an advantage and a liability of the forward method. On the one hand, we gain a better thermodynamic understanding of the system but on the other hand, it is difficult to consider kinetics. The inverse method leads to field-derived kinetic data. The kinetic data are field derived in the sense that any reaction kinetics are lumped into the postulated mass transfer reactions that produce the measured aqueous phase compositions at the final point in the evolution path. In this document, the term inverse method is used narrowly to mean a method that considers only mass transfers between two points such that the final well analytical data are replicated exactly. All else is considered to be part of the forward method.

Either the forward or the inverse method is used to develop a conceptual chemical model of the system, hereafter referred to as a chemical model or a reaction model. Depending on the method used, the chemical model is used to predict as closely as possible, or replicate exactly, the observed or future analytical data at a point. The forward method could develop a generic chemical model for the interaction of a waste solution with geologic sediments. This chemical model could be used in a predictive mode at other sites and would preclude the necessity of developing an individual chemical model (reaction model) for each site. The forward method is the only available alternative at sites where sufficient and appropriate data are unavailable. Use of the forward method would enable a regulatory agency to evaluate a potential area for suitability as a waste disposal site before the fact. The inverse method could only be used at existing sites to develop a reaction model to account for what was observed at the site. This reaction model could then be used in a forward mode to predict future conditions at the operational site. The development of the reaction model is basically a thought process or experiment supplemented by the tools at our disposal. One of these tools is ion speciation/solubility calculations. Another potential tool is reviews of the experimental literature to find documented occurrences of the solid phase, especially for the media being studied. The thought process used in developing the reaction model of the system is based on personal experience and knowledge and includes such factors as kinetics, degree of crystallinity, pH studies, and redox status of the studied system.

CHAPTER 9

MINTEQ INPUT FILES

The sample input file can be divided into four sections. The first section is composed of five lines of user options and certain solution parameters (e.g., temperature). The analytical data for the various components are contained in the second section. Type modifications are designated in the third section. Type modifications involve, for example, declaring that a solid from the MINTEQ data base is present with a finite mass or declaring that a solid is allowed to precipitate if it becomes oversaturated with respect to its solubility product during the modeling run. Species and associated reactions not in the MINTEQ thermodynamic data base are inserted in the fourth section.

For MINTEQ calculations, there are six different types of species that we may enter. These six different types of species are used in sections 2-4 of the input file. Type 1 species are the analytical data. They are commonly referred to as "basis species" or "components." The components are the reactants in the reactions formulated in the MINTEQ thermodynamic data base. In other words, the mass action expressions are written in terms of components. There must be at least one component for every element with analytical data. Redox elements must have a component for every redox state that you wish to represent in the system. For example, iron has two components, Fe^{2+} and Fe^{3+}, to represent the +2 and +3 oxidation states of iron. The components or basis species will not necessarily have the same form as the element they represent; an example of this is arsenic. The H_3AsO_4 component is used to designate the +5 oxidation state of arsenic. The only restriction on the specification of components is that a component cannot be a combination of other components. Oxidation/reduction reactions, as written in MINTEQ, are an exception to this rule. The ID numbers for components represent the alphabetical order of the chemical symbols of the elements in the periodic table. The third number is an arbitrary designation that allows the user to distinguish between the different oxidation states of the same element. The component ID numbers for iron are 280 and 281 to represent the +2 and +3 oxidation states of iron, respectively. Iron is the 28th symbol in the periodic table as determined by alphabetical order. The symbols for ID numbers beginning with 990 are explained in the discussion of the adsorption algorithms. For your convenience, component ID numbers are given in Table 9.1 and in Appendix A.

Type 2 species are aqueous complexes formed by combining components; they are sometimes called "derived" species. For example, the HSO_4^- species is a Type 2 species (complex) that is derived from two components, H^+ and SO_4^{2-}. Data entered in the MINTEQ input file, such as a new adsorption reaction, that

TABLE 9.1. Components in MINTEQ

Component	ID Number	Component	ID Number	Component	ID Number
E	001	Fe^{3+}	281	HSe^-	760
H_2O	002	H^+	330	$HSeO_3^-$	761
Ag^+	020	Hg_2^{2+}	360	SeO_4^{2-}	762
Al^{3+}	030	$Hg(OH)_2$	361	H_4SiO_4	770
H_3AsO_3	060	I^-	380	Sr^{2+}	800
H_3AsO_4	061	K^+	410	Th^{4+}	850
H_3BO_3	090	Li^+	440	Tl^+	870
Ba^{2+}	100	Mg^{2+}	460	$Tl(OH)_3$	871
Br^-	130	Mn^{2+}	470	U^{3+}	890
CO_3^{2-}	140	Mn^{3+}	471	U^{4+}	891
Fulvate	141	MoO_4^{2-}	480	UO_2^+	892
Humate	142	NH_4^+	490	UO_2^{2+}	893
Ca^{2+}	150	NO_2^-	491	V^{2+}	900
Cd^{2+}	160	NO_3^-	492	V^{3+}	901
Cl^-	180	Na^+	500	VO^{2+}	902
Cr^{2+}	210	Ni^{2+}	540	VO_2^+	903
$Cr(OH)_2^+$	211	PO_4^{3-}	580	Zn^{2+}	950
CrO_4^{2-}	212	Pb^{2+}	600	SOH1	990
Cs^+	220	Ra^{2+}	670	SOH2	991
Cu^+	230	Rb^+	680	XPSIO	992
Cu^{2+}	231	HS^-	730	XPSIB	993
F^-	270	S	731	XPSID	994
Fe^{2+}	280	SO_4^{2-}	732	SOHB	995

are not in the MINTEQ data base are entered as Type 2 species. The ID numbers for complexes are 7-digit numbers. The first three digits represent the ID number for the cationic component of the complex, while the second three digits represent the ID number of the anionic component of the complex. The last digit is an arbitrary designation that allows you to distinguish between complexes that contain varying stoichiometries for the same cationic and anionic components. The ID numbers for complexes are found in Appendix B and in the MINTEQ data base.

Species whose activities are fixed are called Type 3 species or "fixed" species. Redox couples are entered as Type 3 species if you want to speciate the redox couples according to an Eh that you have imposed on your system. The activity ratio of the couples is then "fixed" by the imposed Eh. Components whose activity you wish to fix are also called Type 3 species. An example would be fixing the hydronium ion activity if there is a measured pH for the system. Solids and gases may also be declared Type 3 species. This Type 3 designation fixes the activity of the specified gases and solids and means that these phases are in infinite supply in the system.

Type 4 species are solids present in the system in some finite amount. These solids can be entered with a finite mass, which may dissolve during the modeling simulation.

Solids that are allowed to precipitate if they become oversaturated during the modeling simulation are designated Type 5 solids (species) or "dissolved" solids. If Type 4 solids completely dissolve during a modeling simulation, MINTEQ automatically converts them into Type 5 (dissolved) solids. Identification numbers for solids are given in Appendix B. The first two digits in the 7-digit ID number for solids designate the mineralogical class of the solid. This mineral classification system is described in Dana and Ford (1957) and in Robie et al. (1978). The mineral group ID numbers are given in Table 9.2. The next three digits in the mineral or solid phase ID number represent the leading cation in the chemical formula for the mineral or solid. The last two digits are arbitrary designations to distinguish between minerals or solids that would otherwise have the same numbers (e.g., minerals or solids having the same chemical formula but distinct structures).

Type 6 species are ignored by MINTEQ while performing calculations on a given system. Type 6 species may be solids, complexes, or gases; their values are calculated at the end of the simulation and displayed in the output for the information of the user. Certain components, such as the electron, may also be declared Type 6 species. Type 6 species are alternately know as "excluded" species.

TABLE 9.2. Mineral Group ID Numbers

00	elements
10	sulfides, thiosulfates
20	oxides and hydroxides
30	multiple oxides
40	bromides
41	chlorides
42	fluorides
43	iodides
50	carbonates
51	nitrates
52	borates
53	chlorates
60	sulfates
61	selenites, selenates
70	phosphates
72	arsenates
73	vanadates
74	molybdates, molybdites
75	uranates
76	tungstates
80	orthosilicates
82	chain silicates
84	framework silicates
86	sheet silicates
90	acetates
91	oxalates
92	citrates

We will use these 6 species types when creating a file to execute ion speciation/solubility and mass transfer calculations. In this section, we will only deal with the creation of the various input files. The output from the runs will be discussed in Chapter 11. The FORTRAN formats for the different types of input data are listed in the next section, "sample problems," for the benefit of those not requiring further explanation and who desire to use the material for a quick reference. These format fields and abbreviated explanations are taken directly from Felmy et al. (1984b). For those users who have not had extensive experience with the MINTEQ code and/or desire a more detailed explanation, the paragraphs following the format statements go into more detail on the data to be entered for each format field. Additionally, example input files are provided to demonstrate how to set up MINTEQ runs for specific uses.

GENERALIZED DATA FILE FORMAT

SECTION 1

Basic Input Data and FORTRAN Statements

Line 1 (A80)	Alphanumeric description of the sample.
Line 2 (A80)	Alphanumeric description of the sample.
Line 3[a]	Water temperature, analytical units and fixed ionic strength designation.
Line 4 [8(I1, 1X)]	This line contains the run-specific user options.

Option 1. The inorganic carbon input option.
(0) = total inorganic carbon.
(1) = total alkalinity.

Option 2. The debug print option. This is generally used only when modifications have been made to the code, and the values of certain arrays must be checked.
(0) = No debug printout.
(1) = Prints the values of the IDX, C, IDY, GAMMA, C, and Y arrays.
(3) = Prints the NNN, NN(1), NN(2) and the IDY, GK, GK1 arrays in Subroutine KCORR.
(4) = Prints the IDX, X, IDY, L, and GK arrays every iteration in Subroutine SOLID and prints the saturation index for the solid added to the phase assemblage in Subroutine SOLIDX.

Option 3. The charge balance option.
(0) = Terminates execution of the program if the initial charge imbalance is greater than 30%.
(1) = Does not terminate execution regardless of the initial computed charge imbalance.

Option 4. Considered solids and print option.
(0) = Does not allow all of the solids in the data base to recipitate or dissolve. The only solids considered will be those entered in input section 3 under type changes. Print the problem results after the

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[a] This line is free formatted on the VAX version.

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initial aqueous speciation plus solids problem is solved and after all Type 5 solids are either in equilibrium or are undersaturated.

(1) = Allow all solids in the data base to precipitate if they become oversaturated. That is, designate all solids in the data base as Type 5. Print the problem results only after the entire problem has been solved.

(2) = Consider all solids in the data base. Print the problem results after the initial user-specified problem has been solved and again after all Type 5 solids are undersaturated or are in equilibrium.

(3) = Consider all solids in the data base. Print the problem results following the selection of every solid and after all of the solids are in equilibrium or are undersaturated.

Option 5. The total number of iterations option.
(0) - Allow 40 iterations.
(1) - Allow 10 iterations.
(2) - Allow 100 iterations.
(3) - Allow 200 iterations.

The 100 or 200 iteration options should be selected if a large number of solids have been designated as considered solids. The 10-iteration option is only useful when debugging the program.

Option 6. The pH variation option.
(0) = Do not allow the pH to automatically vary during precipitation/dissolution of solid phases.
(1) = Allow the pH to vary during precipitation/dissolution of solid phases. (Note: for this option to work, all solid phases must be declared Type 5 in the initial input.)

Option 7. The fixed ionic-strength option.
(0) = Allow MINTEQ to compute the ionic strength.
(1) = Fix the ionic strength at the value designated on Line 3.

Option 8. The numerical method option.
(0) = Use only Newton-Raphson iteration.
(1) = Use a combination of Newton-Raphson and a modified line search.

Option 9.[a] Output Option

(0) = Do not print an initial listing of the thermodynamic data.
(1) = Print a listing of the thermodynamic data.

Line 5 [I1, 1X, 4(F6.2, 1X)]

This line is for input of adsorption parameters other than the mass total and activity guesses. The first parameter on this line is the adsorption model used (I1 field). The options are

0 = No Adsorption
1 = Activity Kd, Activity Langmuir isotherm, Activity Freundlich Isotherm[a]
2 = Constant Capacitance Double-Layer Model
3 = Triple-Layer, Site-Binding Model.

The next four inputs on this line are

- Solid Concentration (g/L)
- Specific Surface Area (m^2/g)
- Inner-Layer Capacitance (F/m^2)
- Outer-Layer Capacitance (F/m^2)

SECTION 2

Component Input Lines, Line 6+ (I7, 1X, E9.3, 1X, F6.2)

There are as many of these lines as there are components. A blank line must follow the last component. The first specification (I7) is for the component ID number. The second and third specifications are for the analytical mass and the log of the activity guess for the component, respectively.

SECTION 3

Type Modifications

This section is for changing the default species designations. The default type specifications are described under MINTEQ INPUT FILES and in Chapter 3.

The first line of this section contains the first species-type designation and the number of species of this type Format (I3, 1X, I3). The type designations can range from two to six. Then, for each species of the entered type, a line is included (I7, 1X, E9.3, 1X, F6.2) designating information for that species. The first field specification is for the species ID number. Species' ID numbers for components (Type 1) are given in Table 9.1. All other species' ID numbers can be found in Appendix B. The next two specifications are for the new log K and for the enthalpy of reaction. These specifications are both optional and if not included, the default values in the thermodynamic data base are used. A blank line also ends this section. In the case of Type 4 species with an initial mass total (in moles/L), there is an additional input field for the initial mass. This input field follows the input of the enthalpy of reaction resulting in four inputs on one line. The input format for Type IV species is (I7, 1X, E9.3, 1X, F6.2, 1X, E10.3).

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[a] Available only on the VAX version.

SECTION 4

Insertion of Species Not in the Data Base

The first line is for designating the species type and the number of new species of this type (Format I3, 1X, I3). The next lines contain the data for the new species. There are three lines for each species. The first line of species data is in format (I7, 1X, A12, 2F10.4, 2F8.3, 3F5.2, F9.4). The format fields correspond to the following data: ID number, name, enthalpy of reaction, log K, minimum log K, maximum log K, charge, Debye-Hückel A parameter, Debye-Hückel B parameter, and molecular weight, respectively. Only the ID number and log K are essential. For a description of the Debye-Hückel parameters, see Chapter 5.

The second line of data is in format [F5.2, 1X, I1, 1X, 6(F7.3, 1X, I3, 1X)]. The format fields correspond to the carbonate alkalinity factor, the number of components in the reaction, and the stoichiometry and ID number for up to 6 components.

The third line is in format [3(F7.3, 1X, I3, 1X), I1, 3 (F7.3, 1X, I3, 1X)], and the first part of this line allows for the insertion of information for three additional components. The format field, beginning with I1, is for inserting species information into the "B" matrix. Such information is only useful when the component stoichiometries in the mass action expressions are different from the stoichiometries in the mass balance equation. The latter format fields correspond to the number of components in the "B" matrix, stoichiometry of the component, and component ID number. This section is also terminated with a blank line. When choosing species ID numbers for inserted species, be certain that the ID number selected does not match an ID number already in the MINTEQ data base. The problem is usually in determining the last digit for aqueous species and the last two digits for minerals and solids because the first six digits for aqueous species and the first five digits for solids and minerals are determined by rules outlined at the beginning of this chapter. Therefore, you must be certain that the ID numbers selected for the last one digit or last two digits, depending on the species, are higher than the numbers for any species in the data base that have the same ID numbers as the first six digits of your aqueous species or the first five digits of your minerals and solids. A blank line is also inserted at the end of your input file. This means that there will be two blank lines to end the sample input file.

SAMPLE PROBLEMS

PERFORMING ION SPECIATION/SOLUBILITY AND MASS TRANSFER CALCULATIONS

The data we will use in setting up the sample problems and performing the modeling calculations are from the river water test case modified from Nordstrom et al. (1979) (Table 9.3). The river water test case modified from Nordstrom et al. (1979) is reproduced in Table 9.3. Using this test case, we will begin performing ion speciation/solubility for calculations, then proceed to mass transfer calculations, and, finally, adsorption reactions. The significance of ion speciation/solubility calculations, mass transfer calculations, and computations using adsorption algorithms were outlined in previous chapters. Additionally, we outlined the benefits of the various computations and how each computation fits into our overall modeling philosophy. In this section, we will deal with the mechanics of creating input files to perform the different types of calculations that are possible using the MINTEQ geochemical computer code.

GENERAL INPUT INFORMATION

Within the first five lines of your input file, describe the file and the types of calculations that will be performed. This is the first section of the input data. To begin, Lines "1" and "2" contain an alphanumeric description of the data file entered. The file will be created using the modified river water test case data of Nordstrom et al. (1979) is shown in sample input No. 1. This file is modified in that not all of the analyses in the original file are reproduced here, the bicarbonate number is assumed to represent an analytically determined inorganic bicarbonate value, and the Eh was changed from 0.440 to 0.417. Several of the analyses (elements) are excluded because the thermodynamic data for these elements are not in the data base that was originally distributed with the MINTEQ code (Felmy et al. 1984b). The format for entering each of the first two lines in this sample case and for entering the alphanumeric description is A80. Line "3" is in free format and contains information about the temperature, the units in which we wish to express the concentrations of the various solution constituents, and the ionic strength. The temperature is entered in degrees Celsius (°C) (e.g., 9.5 in sample input No. 1). The output is printed as T = 9.5 or whatever the actual temperature of the input file is, but the "T =" is not included in the input file. The entered temperature is followed by a space and then by the concentration units in which we desire to enter the data. The concentration units must be enclosed in quotation marks as in sample input No. 1. The concentration (analytical) units may be entered as "PPM", "MG/L", "MOL", or "MEQ/L". These designations stand for parts per million, milligrams per liter, molality, and

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TABLE 9.3. Test Case Data

River Water		River Water	
Species	mg/L	Species	mg/L
Na	12.0	NH_4	0.144
K	1.4	Fe(II)	0.015
Ca	12.2	Fe(III)	0.0007
Mg	7.5	Mn	0.0044
Si	8.52	Al	0.005
HCO_3	75.2	Zn	0.00049
Cl	9.9	Cd	0.0001
SO_4	7.7	Pb	0.00003
B	0.050	Cu	0.0005
Br	0.006	Ni	0.0018
I	0.0018	Ag	0.00004
F	0.10	As	0.002
PO_4	0.210	Eh (V)	0.417
NO_3	0.898	T°C	9.5
NO_2	0.019	pH	8.01

milliequivalents per liter, respectively. We then leave a space between the input for the analytical units and the term for the ionic strength. If you wish to fix the ionic strength of the solution, you now enter that ionic strength. You enter 0.00 if you wish to let MINTEQ compute the ionic strength. MINTEQ was allowed to compute the ionic strength in sample input No. 1. It is usually preferable to let MINTEQ compute the true ionic strength of the solution after accounting for complexation reactions rather than try and enter an ionic strength based on the concentrations of the various components. In certain situations, fixing the ionic strength may help MINTEQ converge to an answer. The ionic strength is computed by multiplying the molality of a species in solution by the charge of the species squared, over all the species in solution, and then multiplying this number by one-half. As MINTEQ goes through its iterative procedure trying to converge to the answer, the molalities of the species in solution will change with each iteration. The change in the molalities of the species causes the ionic strength of the solution to vary, which in turn affects the activity coefficients (as determined by the Davies or the extended Debye-Hückel equations). Eliminating some of this concurrent

Sample Input No. 1

```
THIS IS THE RIVER WATER TEST CASE MODIFIED FROM NORDSTROM ET AL. (1979).
INORGANIC CARBON OPTION-ELEMENTS NOT IN EPA DATA BASE ARE EXCLUDED.
 9.5 'MG/L' 0.00
 0 0 0 0 2 0 0 0 0
 0   0.00   0.00   0.00   0.00
     500 1.200E+01
     410 1.400E+00
     150 1.220E+01
     460 7.500E+00
     770 2.913E+01
     140 7.397E+01
     180 9.900E+00
     732 7.700E+00
     090 2.860E-01
     130 6.000E-03
     380 1.800E-03
     270 1.000E-01
     580 2.100E-01
     492 8.980E-01
     491 1.900E-02
     490 1.440E-01
     280 1.500E-02
     281 7.000E-04
     470 4.400E-03
     471 0.000E+00
     030 5.000E-03
     950 4.900E-04
     160 1.000E-04
     600 3.000E-05
     230 0.000E+00
     231 5.000E-04
     540 1.800E-03
     020 4.000E-05
     060 3.362E-03
     061 0.000E+00
     001 0.000E+00  -7.43
     330 0.000E+00  -8.01

   3   8
     330 8.01
     001 7.43
2812800
2302310
4714700
4904920
4914920
0600610
```

variation by fixing the ionic strength may sometimes help MINTEQ converge. One should bear in mind, however, that fixing the ionic strength may have a profound effect on the computed results.

Line 4 contains the user options that are specific to each run (see previous discussion under Section 1, basic input data). Customarily, you will enter default values (0) for all options except, occasionally, Options 1 and 5; consequently, we will discuss Options 1 and 5 in greater detail. (Options 2-4 and 6-9 will not be discussed further). It will sometimes be necessary to enter a 2 or 3 for Option 5 to permit the MINTEQ code to iterate a sufficient number of times to converge to an answer; this is particularly important when you are dealing with solids that are precipitating and dissolving. Every time a solid precipitates or dissolves, MINTEQ must go through another series of iterations to speciate and equilibrate the solution. If several solids are specified to dissolve or precipitate, the total number of iterations required by MINTEQ to converge may become quite large.

A "0" or a "1" can be entered for Option 1, the inorganic carbon option. A "0" indicates that you want to enter the inorganic carbon as total inorganic carbon, and a "1" indicates that the analytical data will be entered as an alkalinity value. Both the total inorganic carbon and the total alkalinity are entered as carbonate (CO_3^{2-}). A few examples of the conversion of analytical data to inorganic carbon or alkalinity are provided for your convenience.

Example A

If you have, for example, an analytical value of 61 mg/L HCO_3, you can enter the data in one of two ways:

Option 1 = "0"

Enter CO_3^{2-} = 60/61 x 61 mg/L HCO_3^- = 60 mg/L if entering data as mg/L ("MG/L").

Option 1 = "1"

Enter CO_3^{2-} = 60/61 x 61 mg/L x 1/2 = 30 mg/L.

Example B

If you have data from an alkalinity titration where results are expressed as mg/L of $CaCO_3$, this number must be converted to a carbonate value expressed as inorganic carbon or alkalinity. It wouldn't be correct to use option 1 = "0" unless you knew all the alkalinity was carbonate alkalinity. Let's say that you have an alkalinity value given as 100 mg/L of $CaCO_3$.

Option 1 = "0"

Enter CO_3^{2-} = 100 mg/L $CaCO_3$ x 60/100 x 2 = 120 mg/L.
Option 1 = "1"

Enter CO_3^{2-} = 100 mg/L $CaCO_3$ x 60/100 = 60 mg/L.

The river water test case of Nordstrom et al. (1979), as modified for these examples, has the analytical carbonate expressed as 75.2 mg/L of HCO_3^-. Sample input Nos. 1 and 2 show the proper numbers in mg/L to input as CO_3^{2-} for Option 1 = "0" (73.97) and Option 1 = "1" (36.98), respectively. The same results are obtained regardless of the option used as long as the correct conversions are made.

Line 5 contains the options to define the type of adsorption algorithm that you would like to use. Certain parameters required by the various adsorption algorithms are also included in Line 5. We will discuss in detail the adsorption options in the adsorption section of this manual. Zeros are entered in this line if the adsorption algorithms are not used.

To begin Line 6, the component identification (ID) must be input (I7) along with the analytical mass of each component (1X,E9.3). Component identification numbers are provided in Table 9.1. Component identification numbers may also be found in the file "Comp.dat". The analytical units used to enter the masses must agree with the unit designations on Line 3. When using some of the adsorption algorithms, parameters other than an analytical mass must be inserted. These exceptions will be addressed as we discuss the individual adsorption routines. It is not necessary to enter guesses for the log of the activity (1X,F6.2) of the individual components. If you do not enter an activity guess, MINTEQ will divide the analytical molality by 10 and automatically enter that new number as an activity before beginning the iterative loop that leads to a solution. It is possible to enter activity guesses for the hydronium ion concentration and the electron activity because we know the values for these activities from our measurements (see sample input No. 2). Good activity guesses will help MINTEQ converge to an answer more quickly. For example, sample input No. 3, with activity guesses for all components, converged to an answer after 4 iterations, while sample input No. 2, with no activity guesses, took 20 iterations to reach the same solution.

Certain data must be converted to different forms or numbers before entering these data in the component file just discussed. The redox potential (Eh) in the modified river water test case is given as 0.417 volts (V), while a pe must be entered in the MINTEQ input file. The 0.417 V may be converted to pe (negative log of the electron activity) by dividing the volts by 0.0561 [T = 9.5°C, (or 282.5K) at 25°C divide by 0.0592] to obtain a pe of 7.43 as indicated in Equation (9.1).

Sample Input No. 2

```
THIS IS THE RIVER WATER TEST CASE MODIFIED FROM NORDSTROM ET AL. (1979).
ALKALINITY OPTION-ELEMENTS NOT IN EPA DATABASE ARE EXCLUDED.
9.5 'MG/L' 0.00
1 0 0 0 2 0 0 0 0
0   0.00   0.00   0.00   0.00
     500 1.200E+01
     410 1.400E+00
     150 1.220E+01
     460 7.500E+00
     770 2.913E+01
     140 3.698E+01
     180 9.900E+00
     732 7.700E+00
     090 2.860E-01
     130 6.000E-03
     380 1.800E-03
     270 1.000E-01
     580 2.100E-01
     492 8.980E-01
     491 1.900E-02
     490 1.440E-01
     280 1.500E-02
     281 7.000E-04
     470 4.400E-03
     471 0.000E+00
     030 5.000E-03
     950 4.900E-04
     160 1.000E-04
     600 3.000E-05
     230 0.000E+00
     231 5.000E-04
     540 1.800E-03
     020 4.000E-05
     060 3.362E-03
     061 0.000E+00
     001 0.000E+00  -7.43
     330 0.000E+00  -8.01

   3   8
     330 8.01
     001 7.43
2812800
2302310
4714700
4904920
4914920
0600610
```

Sample Input No. 3

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979)
EH AND PH ARE FIXED-ACTIVITY GUESSES INPUT
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
0   0.00    0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    090 2.860E-01  -5.35
    130 6.000E-03  -7.15
    380 1.800E-03  -7.87
    270 1.000E-01  -5.31
    580 2.100E-01 -10.35
    492 8.980E-01  -4.77
    491 1.900E-02  -5.32
    490 1.440E-01 -17.71
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    470 4.400E-03  -7.19
    471 0.000E+00 -26.30
    030 5.000E-03 -14.84
    950 4.900E-04  -8.41
    160 1.000E-04  -9.32
    600 3.000E-05 -11.46
    230 0.000E+00 -15.25
    231 5.000E-04 -10.47
    540 1.800E-03  -8.76
    020 4.000E-05  -9.68
    060 3.362E-03 -24.97
    061 0.000E+00 -14.74
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   8
    330 8.01
    001 7.43
2812800
2302310
4714700
4904920
4914920
0600610
```

$$pe = volts/(\frac{2.303\ RT}{F}) \qquad (9.1)$$

where R is 1.9872 cal/K-mol, T is temperature in degrees Kelvin, and F is 23,060.9 cal/volt-equivalent. Additionally, several of the original data must be multiplied by factors if the analytical data are not in the same form as the respective components. For example, the arsenic concentration is given as mg/L (0.002) of the elemental form in Nordstrom et al. (1979). The arsenic (III) and (V) components in MINTEQ are entered as H_3AsO_3 and H_3AsO_4, respectively. Therefore, the analytical mass of the elemental form must be multiplied by the ratio of the molecular weights of H_3AsO_4 or H_3AsO_3 to As. It does not matter, theoretically, in which form [(III) or (V)] we enter the arsenic as long as we tell the code to speciate the arsenic between the redox states according to the measured Eh that is imposed on the system. If we impose an Eh (pe) on the system and want information on the redox status of arsenic, both arsenic species must be included in the input file. However, it is only necessary to enter an analytical mass for one of the species.

In the following paragraphs, we will discuss how to tell the MINTEQ code to speciate the redox couples according to the imposed Eh. Let's enter the analytical value of arsenic as H_3AsO_3, as in sample input No. 2. You must divide the molecular weight of H_3AsO_3 by the molecular weight of As and then multiply this number (1.681) by the analytical value of As (0.002). From this you can obtain the value for H_3AsO_3 (3.362×10^{-3}) and enter that value into the input file. If you wanted to enter the As as H_3AsO_4, the multiplier would be slightly larger (1.895) and, thus, the number entered into our input file would also be slightly larger. Alternatively, you could divide the analytical As between the two redox species. The approach you take has no effect on the final solution as long a redox potential (pe) is imposed on the system. Other species in the river water test case that need to have the analytical number changed to comply with the component form include silicon and boron. Water does not have to be inserted as a component by the user. MINTEQ automatically inserts water into the component file. That completes the insertion of components (Type 1 species in MINTEQ terminology).

Type 2 species are only input if the required data are not in the MINTEQ data base. Type 2 species also appear in the MINTEQ output files as complexes.

Leave 1 blank line after the Type 1 species (components) and begin to insert Type 3 species, or species that have fixed activities. Type 3 species include gases whose partial pressures you wish to fix, solids that are present in infinite supply, components whose activities you wish to fix (e.g., pH and pe), and redox reactions between components.

For the first line of this section (Type 3 species), enter the species type (3); leave a space and then enter the number of Type 3 species you want in the data file (I3, 1X, I3). In sample input No. 3, you should enter 8 Type 3 species. The species are entered a line at a time beginning with the species ID number. Next, enter the log K of the reaction and finally, enter the enthalpy of the reaction (I7, 1X, E9.3, 1x, F6.2). Species ID numbers may be found in the MINTEQ thermodynamic data base (Thermo.dat) or in Appendix B. It is mandatory only that the species ID number be included. If values for the log K and enthalpy are not included, the values in the MINTEQ thermodynamic data base are used.

SPECIFIC SAMPLE INPUT FILES

Fixed pH and pe

In sample input No. 3, the pH and pe are fixed at the measured values and these values are included in the log K columns of the Type 3 species. To fix the pH (component ID No. 330) and pe (component ID No. 001), enter the pH and pe in place of the log K values for the Type 3 species. This will mean that the sign has been changed from the activity guesses given the pH and pe in the Type 1 species.

Fixed Partial Pressure of Gases

We have fixed the partial pressure of CO_2 (3301403) at the atmospheric pressure of CO_2 ($10^{-3.5}$ atm) in sample input No. 4. This pressure is entered as a log value of 21.66 and is computed from the reaction for CO_2 from the MINTEQ data base. The reaction involving CO_2 is given as follows:

$$CO_3^{2-} + 2H^+ = CO_2\ (g) + H_2O \tag{9.2}$$

where the log K is 18.16. We then write the reaction as a typical reaction with the products over the reactants equal to the reaction equilibrium constant as in Equation (9.3).

$$\frac{PCO_2\ (H_2O)}{(CO_3^{2-})\ (H^+)^2} = K \tag{9.3}$$

where ( ) (parentheses) represent activities and K is the equilibrium constant for the reaction and PCO_2 is the partial pressure of $CO_2(g)$. By taking log values and incorporating the log of the partial pressure of CO_2 into the log K of the reaction, we find that the new log K for the reaction is equal to 18.16 plus 3.5 or 21.66. This change in values would represent a solution in equilibrium with the carbon dioxide (CO_2) in the atmosphere. Say that you wanted

Sample Input No. 4

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
PCO2 IS FIXED-CO3 EXCLUDED-ACTIVITY GUESSES
9.5 'MG/L' 0.00
0 0 1 0 2 0 0 0 0
0   0.00   0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 0.000E+00  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    090 2.860E-01  -5.35
    130 6.000E-03  -7.15
    380 1.800E-03  -7.87
    270 1.000E-01  -5.31
    580 2.100E-01 -10.35
    492 8.980E-01  -4.77
    491 1.900E-02  -5.32
    490 1.440E-01 -17.71
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    470 4.400E-03  -7.19
    471 0.000E+00 -26.30
    030 5.000E-03 -14.84
    950 4.900E-04  -8.41
    160 1.000E-04  -9.32
    600 3.000E-05 -11.46
    230 0.000E+00 -15.25
    231 5.000E-04 -10.47
    540 1.800E-03  -8.76
    020 4.000E-05  -9.68
    060 3.362E-03 -24.97
    061 0.000E+00 -14.74
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   9
    330 8.01
    001 7.43
3301403 21.66
2812800
2302310
4714700
4904920
4914920
0600610
```

to increase the partial pressure of CO_2 to more closely correspond to values that are found in soils. To increase the partial pressure of carbon dioxide to $10^{-2.5}$ atmospheres, you would add the negative log of this value which is 2.5 to the log K of the reaction (18.16) to obtain a new log K of 20.66. This value would then be entered as the new log K for the reaction involving carbon dioxide. By fixing the partial pressure of carbon dioxide at the atmospheric value, we are representing a system that is open to the atmosphere. If the pressure of carbon dioxide was not fixed, we would be representing a system closed to the atmosphere. If you fix the pH and the partial pressure of carbon dioxide and also enter a value for carbonate as inorganic carbon, the system becomes overconstrained because there are no variables in the Equation (9.2), as the activity of H_2O is also fixed. MINTEQ responds to this by removing the carbonate mass balance equation from the system. In other words, MINTEQ allows the total inorganic carbon to vary to satisfy the pH and carbon dioxide levels that are imposed on the system and ignores the input carbon value. A more valid approach is to fix any two of the three (partial pressure of carbon dioxide, pH, and total inorganic carbon) and allow MINTEQ to compute the third parameter. Sample input No. 4 was constructed in this manner. No mass was entered for inorganic carbon (component ID No. 140) because of the fixed partial pressure of CO_2 and fixed pH. You must, however, make a guess for the log activity of component ID No. 140. The guess for this carbonate activity will usually be close to -5.00. We also had to change the number of fixed species (Type 3) to 9 because of the inclusion of carbon dioxide. Which parameter we allow to vary depends on the confidence we have in our measurement for each parameter.

Fixed Species Activity

The activity of a species can be fixed by entering the ID number as a Type 3 species. Depending on the complexation reactions that occur, entering the ID number as a Type 3 species may alter the total final concentration from the concentration originally entered for a component.

Redox Reactions

Imposed pe. To impose a pe on a reaction, a redox reaction (ID number, Type 3 species) must be entered for the redox species put in equilibrium with the imposed pe. The ID numbers for the redox reactions can be found in the last section of the file "Thermo.dat" and in Appendix B. If a redox reaction is not entered for two redox species, and a mass is entered for only one of the redox species of that couple in the component file (Type 1 species), then MINTEQ will not distribute the mass entered for that redox species (i.e., one of the redox species will continue to have a mass of 0.00). However, if, for example, you enter a redox reaction for the Fe^{3+}/Fe^{2+} couple (ID 2812800), only a mass for the Fe^{3+} or the Fe^{2+} species will then need to be entered, as long

047

as you have imposed a pe (Type 3 species). MINTEQ will calculate the activity of the other species. It will sometimes help convergence if the analytical mass is entered for the dominant species. In sample input No. 4, we have entered redox reactions for iron, copper, manganese, nitrogen, and arsenic. These redox species will be speciated according to the pe (7.43) imposed on the system. Sometimes it is beneficial to split the total analytical mass of an element among its various redox species even when a redox reaction for the redox species of that element is entered. Entering the analytical mass this way is sometimes helpful if one of the redox species of the element in question is causing the following error message to occur: "a component X is 0.0;" this is discussed in more detail in the section on error messages. The total concentrations of the redox elements have been partitioned among the redox species in sample input No. 5 (from analytical data for redox species found in Table 9.3).

There is another way to impose a redox potential on the water sample you are modeling. Instead of entering an Eh (pe) measured by a platinum electrode, enter analytical masses for an "indicator" redox and let MINTEQ calculate the speciation of additional redox species according to the redox potential imposed by the ratio of the analytical masses of the indicator redox species. MINTEQ calculates this number by a slightly circuitous route. First, remove the pe from the Type 3 species and declare the pe to be a Type 6 species, as in sample input No. 5. Then enter, as a Type 3 species, the ID number for the redox species you wish to let impose a pe on the whole system, and analytical masses for the two components in the redox couple. In sample No. 5, we have designated the Fe^{3+}/Fe^{2+} couple (2812800) as the control of the Eh (pe) of the system. After designating the iron couple as the pe control and entering masses for Fe^{2+} and Fe^{3+}, (you may also enter all of the mass in one of the redox couples because the pe is fixed) run MINTEQ and let it calculate the pe of the system as determined by the iron redox couple. In the second step of the modeling, you must take the pe calculated by the iron redox couple (1.2995) and enter that pe as a Type 3 species in another run similar to those runs with a fixed pH and pe (see sample input No. 6). Entering the electron as a Type 3 will also involve removing the electron from the Type 6 species. The additional redox couples must also be added to the Type 3 species, and MINTEQ will then speciate these additional couples according to the pe determined by, for example, the iron redox couple (sample input No. 6). Using a redox couple to fix the pe might be a satisfactory approach for those systems in which you are confident of the analysis for the redox species of an element. You must also be confident that the redox species are in equilibrium with the groundwater. Lindberg and Runnells (1984) have addressed the problem of the internal disequilibrium of redox reactions. It is not sufficient to initially declare an "indicator" a Type 3 species and the pe a Type 6 species and leave other redox species out of the Type 3 designation. This problem setup will not cause the other redox couples to be speciated, because you have not declared them as

Sample Input No. 5

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979)
EH DETERMINED BY FE-PH FIXED-ELEMENTS NOT IN DATA BASE ARE EXCLUDED
9.5 'MG/L' 0.00
0 0 1 0 2 0 0 0 0
0   0.00   0.00    0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    090 2.860E-01  -5.35
    130 6.000E-03  -7.15
    380 1.800E-03  -7.87
    270 1.000E-01  -5.31
    580 2.100E-01 -10.35
    492 8.980E-01  -4.77
    491 1.900E-02  -5.32
    490 1.440E-01 -17.71
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    470 2.200E-03  -7.19
    471 2.200E-03 -26.30
    030 5.000E-03 -14.84
    950 4.900E-04  -8.41
    160 1.000E-04  -9.32
    600 3.000E-05 -11.46
    230 2.000E-04 -15.25
    231 3.000E-04 -10.47
    540 1.800E-03  -8.76
    020 4.000E-05  -9.68
    060 1.681E-03 -24.97
    061 1.895E-03 -22.00
    001 0.000E+00  -1.23
    330 0.000E+00  -8.01

  3   2
    330 8.01
2812800
  6   1
    001
```

Sample Input No. 6

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979)
EH DETERMINED BY FE-PH FIXED-ELEMENTS NOT IN DATA BASE ARE EXCLUDED
9.5 'MG/L' 0.00
0 0 1 0 2 0 0 0 0
0   0.00   0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    090 2.860E-01  -5.35
    130 6.000E-03  -7.15
    380 1.800E-03  -7.87
    270 1.000E-01  -5.31
    580 2.100E-01 -10.35
    492 8.980E-01  -4.77
    491 1.900E-02  -5.32
    490 1.440E-01 -17.71
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    470 2.200E-03  -7.19
    471 2.200E-03 -26.30
    030 5.000E-03 -14.84
    950 4.900E-04  -8.41
    160 1.000E-04  -9.32
    600 3.000E-05 -11.46
    230 2.000E-04 -15.25
    231 3.000E-04 -10.47
    540 1.800E-03  -8.76
    020 4.000E-05  -9.68
    060 1.681E-03 -24.97
    061 1.895E-03 -22.00
    001 0.000E+00  -1.23
    330 0.000E+00  -8.01

  3   8
    330 8.01
    001 1.2995
2812800
2302310
4714700
4904920
4914920
0600610
```

Type 3 species. If you initially declare the indicator species and the other redox couples as Type 3 species and leave the pe as a Type 6 species, then the pe that is calculated is meaningless. The pe calculated will have no meaning because MINTEQ will calculate the pe based on the ratio of the masses of each of the redox species. You will probably not have masses of the redox species for each element and even if you did, the natural redox system will undoubtedly be in internal disequilibrium.

Dissolution and Precipitation of Solid Phases

Solids that are allowed to dissolve or precipitate are designated as Type 4 and Type 5 solids, respectively. Type 4 solids are solids that are initially present in some finite mass that you designate in the input. Type 5 solids are solids from the MINTEQ data base that are allowed to precipitate to satisfy their solubility product if they become oversaturated during the modeling simulation.

The input format for Type 4 solids (species) is (I7, 1X, E9.3, 1X, F6.2, 1X, E10.3). The first input field specification is for the ID number of the solid. The second and third format field specifications are for the log K and the enthalpy of reaction, respectively. Values will be entered in these fields only if you wish to change the log K and enthalpy values from those in the data base. The last field (E10.3) is reserved for entering the initial number of moles of the solid (per kilogram of solution) in the system modeled. The input field and data entry for Type 5 species, is identical to that for Type 4 species except that the last input field is absent. With Type 5 solids, the dissolved solids that can precipitate are considered, therefore, there is no need to add a mass.

Sample input No. 7 is an example of the river water test case that was modified to include the precipitation and dissolution of solid phases. Type 4 solids are precipitated solids that exist in finite masses and can dissolve. In sample input No. 7, calcite (5015001) was included as a precipitated solid with a finite mass (0.1 moles). Ferrihydrite (202810), gypsum (6015001), and amorphous silicon dioxide (2077004) are included as Type 5 solids that are allowed to precipitate if they become oversaturated during the modeling simulations. Identification numbers for solids, minerals, complexes, and redox species may be found in Appendix B. The problem setup shown in sample input No. 7 simulates the contact of the river water solution with 0.1 moles of calcium carbonate. You might use calcium carbonate to represent a sediment through which the river water is percolating. If there is an excess of calcium carbonate, you could enter the calcium carbonate as a Type 3. Calcium carbonate would then always be available for dissolution to the equilibration point, no matter how much had previously dissolved. We entered a new log K for gypsum (4.6) in sample input No. 7. If no entries are made in these columns, the values in the MINTEQ thermodynamic data base are used. Ferrihydrite was the

051

Sample Input No. 7

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
CONTACTING TYPE 4 AND 5 SOLIDS-ELEMENTS NOT IN DATA BASE ARE EXCLUDED.
9.5 'MG/L' 0.00
0 0 1 0 2 0 0 0 0
0   0.00   0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    090 2.860E-01  -5.35
    130 6.000E-03  -7.15
    380 1.800E-03  -7.87
    270 1.000E-01  -5.31
    580 2.100E-01 -10.35
    492 8.980E-01  -4.77
    491 1.900E-02  -5.32
    490 1.440E-01 -17.71
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    470 2.200E-03  -7.19
    471 2.200E-03 -26.30
    030 5.000E-03 -14.84
    950 4.900E-04  -8.41
    160 1.000E-04  -9.32
    600 3.000E-05 -11.46
    230 2.000E-04 -15.25
    231 3.000E-04 -10.47
    540 1.800E-03  -8.76
    020 4.000E-05  -9.68
    060 1.681E-03 -24.97
    061 1.895E-03 -22.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   8
    330 8.01
    001 7.43
2812800
2302310
4714700
4904920
4914920
0600610
  4   1
5015001                  1.00E-01
  5   3
2028100
6015001 4.60
2077004
```

only iron solid to become saturated and precipitate during the modeling run. The pH and pe were fixed at the analytical values, and the redox reactions indicated by the Type 3 declarations were considered.

Variable pH and pe

Allowing the pH and pe to vary according to the precipitation/dissolution, ion speciation, and redox reactions that take place can be useful. For example, you may want to see how the pH and pe change when a solution is contacted with an assemblage of minerals used to represent natural sediments.

Variable pH

To permit the pH to vary, enter a mass for the total hydrogen in the component file (1.258×10^{-3} in our example). To obtain this total mass of hydrogen, first, speciate the original river water test case (see sample input No. 1); then go to the output where the aqueous mass and sorbed mass of each component are listed. The totals for the aqueous and sorbed masses immediately follow the percent distribution of species. Next, take the total for the mass (in this example, there will only be an aqueous mass) of the hydrogen that is given (1.258×10^{-3} moles/L) and add it to the hydronium ion concentration calculated from the pH ($10^{-8.01}$ moles/L) of the solution and the activity coefficient. The activity of the hydronium ion is calculated from the pH. This activity must be divided by the activity coefficient to give you the hydronium ion concentration. In this case, the hydrogen calculated from the pH is insignificant compared to the mass of complexed hydrogen. At lower pH values, this mass of hydrogen may not be insignificant, and the mass of hydrogen computed from the pH may predominate. The mass of hydrogen listed under the heading "AQUEOUS MASS" only includes hydrogen that is complexed with other species; it does not include the mass of the bare hydronium ion. The summation of both the hydrogen complexed with other species and the bare hydronium ion must be entered in the input file to accurately recompute the pH (see sample input No. 8). Occasionally, the aqueous mass of hydrogen will be a negative number and the sum of this negative number and the moles of hydronium ion in solution will be a negative number. This negative number must be entered in the component file for the total mass of hydrogen. The total amount of hydrogen represents the excess (if positive) or deficiency (if negative) of the hydrogen ion relative to the amount obtained by dissociation of water. If the value is positive, the excess hydrogen ion is available to complex with other components. If the value is negative, excess OH^- is present. This convention, called the proton condition, is used to replace the water mass balance equation. Because of the great excess of H_2O over both H^+ and OH^- in aqueous solution, MINTEQ keeps track of the excess or deficiency of the amount of H^+ relative to the amount to be expected from dissociation of water. Also, recognize that the aqueous mass is given in moles/L, so you must do a conversion if

Sample Input No. 8

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EH AND PH VARIABLE-ELEMENTS NOT IN DATA BASE ARE EXCLUDED
9.5 'MOL' 0.00
0 0 0 0 2 0 0 0 0
0   0.00   0.00   0.00   0.00
    500 5.221E-04  -3.3
    410 3.581E-05  -4.47
    150 3.044E-04  -3.61
    460 3.085E-04  -3.60
    770 3.031E-04  -3.52
    140 1.233E-03  -5.66
    180 2.793E-04  -3.58
    732 8.017E-05  -4.21
    090 4.626E-06  -5.35
    030 7.510E-08  -7.15
    380 1.419E-08  -7.87
    270 5.264E-06  -5.31
    580 2.212E-06 -10.35
    492 1.786E-05  -4.77
    491 5.018E-06  -5.32
    490 2.068E-18 -17.71
    280 4.461E-12 -11.45
    281 2.812E-07 -17.45
    470 8.010E-08  -7.19
    471 7.674E-27 -26.30
    030 1.853E-07 -14.84
    950 7.497E-09  -8.41
    160 8.898E-10  -9.32
    600 1.448E-10 -11.46
    230 5.894E-16 -15.25
    231 7.870E-09 -10.47
    540 3.066E-08  -8.76
    020 3.709E-10  -9.68
    060 1.102E-25 -24.97
    061 2.670E-08 -22.00
    001 0.000E+00  -7.43
    330 1.258E-03  -8.01

  3   6
2812800
2302310
4714700
4904920
4914920
0600610
  6   1
    001
```

entering your input data in the component file (Type 1) in any other units. It is advisable to use the procedure outlined above and not use Option No. 6 when allowing the pH to vary.

Variable pe

To permit the pe to vary, you must again use the original output (sample input No. 1) from the speciated river water case and look at the section of the output that contains the aqueous masses of the components. The aqueous mass given in this section must be entered for each component in the Type 1 species file (excluding hydrogen, which may differ from this table by the activity of the hydrogen ion as measured by the pH electrode). Remember that the Type 1 species (components) file is just the part of our input file where you enter your analytical masses for the various elements; this means that you enter a mass for each redox couple as determined by the pe of the original solution. By entering the masses speciated according to the initial pe value imposed, you should be able to reproduce that pe when the solution is rerun and the pe is allowed to vary. It is convenient to enter the data in moles/L at this stage (because the output masses are in moles/L) even though the original values may be given in mg/L. The data were entered in moles/L in sample input No. 8. It is advisable to speciate this new input file to establish that the original pe is regenerated, and that the pH, if you have entered masses for the hydronium ion, is also regenerated. If the original pH and pe are obtained, you are ready to let the solution react with solids and minerals, thus permitting the pH and pe to vary according to those reactions. Sample input No. 8 contains the pH and pe as variables (pe must be entered as a Type 6 species), and all analytical data are entered (as previously described) to ensure that the pH and pe are reproduced. The original pH and pe were reproduced with this input file. If you only want the pe to vary, fix the pH as before and do not enter a mass for the hydronium ion. The masses for the redox species must be entered as explained previously.

We are now ready to react our solution with an assemblage of solid phases to let the pH and pe change according to the precipitation/dissolution, complexation, and redox reactions that occur. In sample input No. 9, we have set up an input file that will react the solution with the same solids described in sample input No. 7; this will permit the pH and pe to vary according to the reactions that occur. The new pH and pe calculated were 8.57 and 6.86, respectively. Remember that the original pH and pe values were 8.01 and 7.43, respectively. By dissolving calcium carbonate in this system, we have raised the pH and precipitated ferrihydrite (amorphous ferric hydroxide). The pe has decreased because the precipitation of ferrihydrite has removed Fe^{3+} from solution and decreased the Fe^{3+}/Fe^{2+} ratio.

Sample Input No. 9

```
THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EH AND PH VARIABLE-ELEMENTS NOT IN THE DATA BASE ARE EXCLUDED.
9.5 'MOL' 0.00
0 0 0 0 2 0 0 0 0
0    0.00    0.00   0.00   0.00
     500 5.221E-04  -3.3
     410 3.581E-05  -4.47
     150 3.044E-04  -3.61
     460 3.085E-04  -3.60
     770 3.031E-04  -3.52
     140 1.233E-03  -5.66
     180 2.793E-04  -3.58
     732 8.017E-05  -4.21
     090 4.626E-06  -5.35
     130 7.510E-08  -7.15
     380 1.419E-08  -7.87
     270 5.264E-06  -5.31
     580 2.212E-06 -10.35
     492 1.786E-05  -4.77
     491 5.018E-06  -5.32
     490 2.068E-18 -17.71
     280 4.461E-12 -11.45
     281 2.812E-07 -17.45
     470 8.010E-08  -7.19
     471 7.674E-27 -26.30
     030 1.853E-07 -14.84
     950 7.497E-09  -8.41
     160 8.898E-10  -9.32
     600 1.448E-10 -11.46
     230 5.894E-16 -15.25
     231 7.870E-09 -10.47
     540 3.066E-08  -8.76
     020 3.709E-10  -9.68
     060 1.102E-25 -24.97
     061 2.670E-08 -22.00
     001 0.000E+00  -7.43
     330 1.258E-03  -8.01

  3   7
2812800
2302310
4714700
4904920
4914920
0600610
5015001
  5   3
2028100
6015001
2077004
  6   1
    001
```

USE OF THE ADSORPTION ALGORITHMS

The creation of the basic input file needed to model ion speciation/solubility calculations is explained at the beginning of this chapter (MINTEQ INPUT FILES). Only the modifications to that file that are necessary to use the adsorption algorithms are covered in this section. One of the changes to the basic input file involves creating a data base for the adsorption reactions you want to model. This change is necessary because there are no data for adsorption reactions in the MINTEQ data base (comparable to those for modeling dissolution/precipitation reactions, for instance). Enter these adsorption reactions as Type 2 species (Type 2 declaration). This Type 2 declaration should immediately follow any other type declarations in our input file. You must, however, insert 1 blank line between any other type declaration and our Type 2 declarations.

Insertion of Reactions

There are minimally four lines that need to be added to the input data file to enter any of the adsorption reactions. The format of the first line of the Type 2 species is (I3, 1X, I3) and is the same format that is used when making Type 3, 4, or 5 declarations. This line indicates the species type and the number of new species of this type. The first number to enter is 2 in column 3, because the adsorption reactions must be entered as Type 2 species. In columns 5-7, enter the number of adsorption reactions you wish to include in your modeling exercise. Three additional data lines must then be entered for every adsorption reaction included in your input data files. In other words, for every three lines of data entered (beyond the initial line) for the adsorption reactions, the number of species must be increased by one. This format is different from the ion speciation/solubility and mass transfer modeling performed at the beginning of this chapter. When performing solubility/mass transfer calculations, every time a new species for Types 3, 4, or 5 is entered, the new line constitutes a new species.

The first of the three data lines is formatted as follows: (I7, 1X, A12, 2F10.4, 2F8.3, 3F5.2, F9.4). These parameters in order are the ID number of the reaction, the name of the species formed, the enthalpy of the reaction, the log K of the reaction, minimum log K, maximum log K, charge, Debye-Hückel A parameter, Debye-Hückel B parameter, and the molecular weight, respectively. Minimally, two of these parameters must be specified; they are the ID number of the reaction and the log K of the reaction. All other information in this line is optional. Minimum and maximum log K's may be inserted into the data base if you wish to have a record or be reminded of the variability of the data that you are using. Limited information is available in the literature for the Debye-Hückel A and B parameters. If the Debye-Hückel A and B parameters are not included in the input file, MINTEQ defaults to the Davies equation for calculating the required single ion activity coefficients. The molecular weight is necessary to make accurate conversions among the concentration units that are input.

The second of the three data lines is formatted: F5.2, 1X, I1, 1X, 6(F7.3, 1X, I3, 1X). This format corresponds to the carbonate alkalinity factor, the number of distinct components in the reaction, and the stoichiometry and ID numbers for up to six separate components. It is imperative to add the carbonate alkalinity factor if the inorganic carbon value in the input file is entered as an alkalinity value. If the inorganic carbon value is entered as inorganic carbon, then the carbonate alkalinity factor is not used and may, therefore, be omitted.

The third data line is formatted 3(F7.3, 1X, I3, 1X), I1, 3(F7.3, 1X, I3, 1X). The first part of this line allows you to insert three additional components if the reaction entered requires it. The second part of the format field, beginning with I1, is for supplying information to the "B" matrix. The information conveyed in this part of the format field describes the number of components in the "B" matrix, the stoichiometry of the component, and the component ID number, respectively. It is necessary to supply additional information to the "B" matrix only if the stoichiometries in the mass action expression differ from the stoichiometries in the mass balance expression. (See the section on the surface complexation models.)

In discussing the adsorption algorithms, a detailed description of input files for a specific algorithm will be given, followed by a brief summary. Thus, if you are already somewhat familiar with the formation of the input file for a particular algorithm, go directly to the summary given at the end of that section.

Using the Activity Kd Model of Adsorption

The activity Kd is applicable over a wider range of natural water compositions than is the Kd determined by concentrations. The activity Kd accounts for changes in aqueous complexation with changing ionic strength and solution composition, while the concentration dependent Kd does not take these effects into account. However, a number of important limitations are inherent in the Kd approach. For example, the number of surface sites is assumed to be greatly in excess. This excess of surface sites implies that there is no mass balance on surface sites. Additionally, electrostatic interactions and the reaction of species, other than the adsorbing species, with the surface site are not considered. Moreover, the effect of ionic strength and pH on the surface properties of the adsorbing solid are not considered. The activity Kd approach is an adequate model of adsorption if the concentrations of the adsorbing metals are low, and the pH and ionic strength are relatively constant.

There are four steps to follow in constructing an input file to model adsorption using the activity Kd. The steps are indicated by arrows on the sample input files (see sample input No. 10). For the first step, enter a 1 in the first column of Line 5. Line 5 contains information for some of the input parameters for adsorption (see section in Generalized Data File Format). The first parameter on this Line (I1) tells the computer which adsorption algorithm you are using. The 1 in the first space of Line 5 allows you to use the activity Kd model of adsorption. To use the activity Kd, it is not necessary to enter any additional information on this line.

For the second step, enter a new component in the Type 1 species file. The Type 1 species file is where the components are input into file Nos. 1-9. These components correspond to the data supplied in our chemical analysis of the aqueous sample. The component you must enter is for the type of adsorption site. There are component identification numbers (ID) for two types of adsorption sites in the MINTEQ data base. These two types of sites are designated as SOH1 and SOH2. The numbers 1 and 2 at the end of the identification numbers are to distinguish between the two types of sites and have nothing to do with the stoichiometry of the adsorption site. For convenience, assume the adsorption sites for the activity Kd have a charge of negative 1 and have the corresponding ID numbers 990 and 991. The component designations, however, will remain SOH1 and SOH2. The designation, SOH, will indicate that SOH1 or SOH2 may be used. You may want to use the two types of sites to let your species adsorb on two different solids with different affinities for the adsorbing species. For our example, we used a single type of adsorption site or solid and use the 990 ID number. This component (990) is entered with the other Type 1 species (components), as shown in sample input No. 10. Zero is entered for the mass of this adsorption site. The activity of the adsorption site is given unit activity, as indicated in sample input No. 10, because with an excess of adsorption sites, the variability of SOH1 (990) is negligible. For the adsorption site (990), MINTEQ does not consider the activity guess to be the log of the activity, but will keep the activity at 1.00 if using the Kd adsorption algorithm. If you insert a zero (i.e., leave the activity blank for the activity guess) you will still get a 1.00 for the activity of the adsorbent. Sample input No. 10 further modifies the river water test case used previously in input files No. 1-9 (Nordstrom et al. 1979). The further modification consists in the elimination of several components to reduce the size of the file.

For the third step, enter component 990 as a Type 3 species. Entering the adsorption site as a Type 3 species means that we have an infinite supply of solid (i.e., the adsorption is not limited by the quantity of solid). It is not required to enter data for a new log K or for the enthalpy (DH) of a reaction for the adsorption site.

Sample Input No. 10

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979) EXAMPLES OF
ADSORPTION USING THE KD ALGORITHM.
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
1   0.00   0.00     0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    990 0.000E+00   1.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   4
    330 8.01
    001 7.43
2812800
    990

  2   2
9901400 K-SOH1            0.000      1.500
0.00  2     1.000 410   1.000 990

9901500 CA-SOH1+          0.00       1.500                  1.00
0.00  2    1.000 150   1.000 990
```

The fourth and final step is the creation of the adsorption data base. The format for these data and the significance of each format field was explained in the preceding section on "Insertion of Reactions." Sample input No. 10 illustrates an input file to model the adsorption, of uncomplexed calcium and potassium ions. The only significant difference between the input data for the two species is that when modeling calcium adsorption, you enter a plus one for the charge. The calcium with a charge of +2 forms a positively charged species when adsorbed on an adsorption site with a negative charge of 1. The positively charged potassium ion and negatively charged adsorption site form a neutral species and it is, therefore, not necessary to enter a charge for this species.

The reaction modeled is

$$\mathrm{SOH1} + \mathrm{M}^{n+} \rightleftarrows \mathrm{SOH1\text{-}M}^{n+} \qquad (9.4)$$

where SOH1 is the adsorption site of constant unit activity, M^{n+} is the aqueous species that is adsorbing, and $SOH1\text{-}M^{n+}$ signifies the adsorption complex where the aqueous species adsorbed onto our adsorption site or solid. The component SOH1 is the designation for a solid surface. In the case of the Kd adsorption algorithm, the H has no significance and does not participate in the chemical reaction. Remember, the SOH1 sites are assumed to be in infinite supply because of the Type 3 designation. The theoretical Kd assumes an excess of adsorption sites over the adsorbate.

The only procedure that is not entirely staightforward in using the activity Kd occurs in the fourth and final step (i.e., creation of the adsorption data base). The log of the adsorption constant, log Kd (used in MINTEQ), is not the conventional Kd that you encounter in the literature. The Kd that is used in MINTEQ is dimensionless and is an activity Kd, while the conventional Kd has the units of mL/g or L/kg and deals with concentrations instead of activities. Before you can enter a Kd value into the MINTEQ data base, you must convert the conventional Kd into an activity Kd. To compute the activity Kd, you must know the activity in solution of the ion that is adsorbing. The computation of the activity of the ion that is adsorbing requires calculations using knowledge of the Kd experiment or, alternatively, activity estimations of the adsorbing species using a knowledge of the speciation of the element of interest.

The following is a short discussion of one way to use information from a Kd experiment to calculate an activity Kd. The experimental information you need is 1) the experimental Kd value, 2) the solution/solid ratio, and 3) the initial (total or analytical) concentration of the adsorbate that you are considering. Using this information and Equation (9.5) it is possible to calculate the equilibrium solution concentration of all species of the adsorbate under consideration.

$$\mathrm{SOLN_c\ (mg/L) = TOT_c\ (mg/L) - (Kd/[Kd + SSR]) \times TOT_c\ (mg/L)} \qquad (9.5)$$

where $\mathrm{SOLN_c}$ = the equilibrium solution concentration of all species of the adsorbate after adsorption occurs
$\mathrm{TOT_c}$ = the total concentration of all species of the adsorbate before adsorption occurs (initial total concentration)
SSR = the solution/solids ratio in mL/g
Kd = the Kd adsorption algorithm in (mL/g)

If the original experiment were conducted in 1000 ml of water containing 100 mg of the adsorbing solid, the solution/solid ratio (SSR) would be 10 ml/mg.

With the equilibrium solution concentration of all species of the adsorbate, you can then compute the activity of the particular adsorbing species to be modeled. Calculating the activity of the adsorbing species to require running MINTEQ with the resulting composition of the solution used in the experiments ($\mathrm{SOLN_c}$), or a similar composition, where $\mathrm{SOLN_c}$ is the total aqueous adsorbate concentration. Alternatively, you can estimate the activity of the adsorbing species from a knowledge of the solution chemistry. The output will express the solution activity of the adsorbing species (A_{as}) in moles/L (M/L).

The next step is to calculate the equilibrium concentration of the adsorbate on the solid using Equation (9.6) or to subtract the solution concentration ($\mathrm{SOLN_c}$) from the original concentration of the adsorbate (TOTc) before adsorption occurs.

$$\mathrm{SLD_c = (Kd/[Kd + SSR]) \times TOT_c\ (mg/L)] \times 10^{-3} \times MW^{-1}} \qquad (9.6)$$

where SLDc is the total concentration of the adsorbate on the solid and MW is the molecular weight of the adsorbing species. Equation (9.6) converts the concentration on the solid from mg/L to moles/L because the output activity of the adsorbing species is expressed in moles/L. The activity Kd is then calculated by

$$\mathrm{Activity\ Kd = SLD_c\ (M/L)/\ A_{as}\ (M/L)} \qquad (9.7)$$

The log of this activity Kd is the value you enter into the MINTEQ data file to represent the log K of the adsorption reaction. Sample input No. 10 has a hypothetical Kd solely to demonstrate file construction.

If species other than components are to be considered as the adsorbing species, then reactions must be added together so that the reaction is still written in terms of components. For example, suppose that you wish to let the $CaOH^+$ species adsorb. To formulate this reaction in terms of the calcium component (Ca^{2+}) will require the addition of the hydrolysis reaction for calcium (Ca^{2+}) and the reaction for $CaOH^+$ adsorbing onto the surface site (SOH). When these two reactions are added together, the following reaction occurs:

$$Ca^{2+} + H_2O + SOH \rightleftharpoons SOH - CaOH^+ + H^+ \tag{9.8}$$

In this manner, the reaction for the adsorption of $CaOH^+$, in terms of components that are in the MINTEQ data base is formulated. The log of the Kd that is entered into the MINTEQ data base is the log Kd of the adsorption of $CaOH^+$ modified by the log K for the hydrolysis of Ca^{2+}.

There is a simple mathematical alternative to the approach previously outlined. In that approach, you were required to speciate the solution in contact with the solid to obtain the activity of the adsorbing species. Alternatively, you can hand calculate the species activity by using the conventional Kd, the association constants for species that contribute significantly to the total aqueous concentration, and the total molality of the species in the solution contacting the solid.

Summary

Step 1: Enter a 1 in the first column of line 5 to indicate the adsorption algorithm used.

Step 2: Enter a new component (990 or 991) to represent the adsorbing solid.

Step 3: Enter the new component (adsorbing solid) as a type 3 species (infinite solid).

Step 4: Create the adsorption data base by entering a minimum of an ID number for the complex formed by the adsorbing species and a log K and stoichiometry for the adsorption reaction.

Using the Activity Langmuir Model of Adsorption

The Langmuir equation has an advantage over the Kd adsorption equation because the Langmuir equation defines a finite limit (S_T) to the adsorption on a given array of sites that meet the Langmuir model criteria. The Langmuir equation makes the following assumptions:

- there is a constant energy of adsorption that is independent of the extent of surface coverage (i.e., a homogeneous surface)
- no interaction occurs between adsorbate molecules.
- only a finite number of sites can adsorb (a monolayer).

To use the activity Langmuir model of adsorption, follow the same steps used in setting up an input file for the activity Kd algorithm. Begin Step 1 by entering a 1 in the first column of Line 5 (see sample problem No. 11).

For Step 2, specify the adsorbent as SOH1 (ID No. 990) or as SOH2 (ID No. 991). In using the activity Langmuir adsorption isotherm, do not enter the adsorbent (990 or 991) component as a Type 3 as we did with the Kd adsorption isotherm. The component is not entered as a Type 3 because there is not an excess of adsorption sites, as in the activity Kd. Enter a mass for the surface sites in step 2, then enter a total mass for the adsorption sites in moles/kg of solvent. The mass of the surface sites is read by MINTEQ as moles/kg of solvent, even though the rest of the data may be input in other concentration units (e.g., mg/L in Sample Input No. 11). The specification of mass in the activity Langmuir isotherm conveys an advantage over the Kd-type approach in that it enables MINTEQ to consider a mass balance on the surface sites. At relatively high concentrations of adsorbate, where most of the surface sites are occupied, the Langmuir sorption model will probably give more reliable results than the Kd sorption model.

For Step 3, create an adsorption data base. As shown in sample problem No. 11, the data file has the same input parameters as the file created for the activity Kd model. Here, before you can enter a log K for the adsorption reaction, you must compute an activity Langmuir constant. The Langmuir equation can be expressed as

$$SLD_C = K_L \ SOLN_C \ S_T/(1 + K_L \ SOLN_C) \tag{9.9}$$

where SLD_C = is the total concentration of the adsorbate on the solid (adsorbent) in molality per unit weight of adsorbent
K_L = the Langmuir constant that defines the binding strength
$SOLN_C$ = the equilibrium concentration of the dissolved adsorbate
S_T = the maximum amount of adsorbate that can be adsorbed

If each adsorbing species occupies one adsorption site, then S_T is also equal to the total number of adsorbing species. Applicability of the Langmuir

Sample Input No. 11

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EXAMPLE OF ADSORPTION USING THE LANGMUIR ADSORPTION ALGORITHM.
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
1   0.00   0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    990 0.100E+00   0.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   3
    330 8.01
    001 7.43
2812800

  2   2
9901400 K-SOH1           0.000      1.500
0.00  2    1.000 410   1.000 990

9901500 CA-SOH1+         0.00       1.500                 1.00
0.00  2    1.000 150   1.000 990
```

equation to modeling a particular set of data is conveniently tested by putting Equation (9.8) in its linear form and plotting experimental data

$$SOLN_c/SLD_c = 1/(K_L \cdot S_T) + SOLN_c/S_T \qquad (9.10)$$

A plot of $SOLN_c/SLD_c$ versus $SOLN_c$ yields a straight line with a slope of $1/S_T$ and intercept of $1/(K_L \cdot S_T)$, if the Langmuir equation is valid. The Langmuir constant (K_L) is obtained by dividing the slope by the intercept.

The reaction in MINTEQ, however, requires that the log K value be the activity Langmuir constant. Therefore, you must substitute the activity of the particular form of adsorbing species (A_{as}) for the total concentration of the adsorbing species ($SOLN_c$) in Equations (9.9) and (9.10). This substitution process will require running MINTEQ with an input consisting of the resulting solution composition, or a similar solution, from the experiments that determined the original Langmuir constant. Alternatively, you can again estimate the activity of the sorbing species from a general knowledge of the speciation of the element of interest. Using the activity of the sorbing species, the activity Langmuir constant is calculated by replotting the data according to Equation (9.10) with $SOLN_c$ substituted by the activity of the adsorbing species. The log of the activity Langmuir constant (K_L) is then inserted for the Log K value in the reaction. The stoichiometry values of 1.000 for component numbers 990 and 410, in sample input number 11, indicate that you have a mass action expression where 1 adsorption site combines with one K^+ to form the adsorption complex (SOH-K). Competition between competing ions can be considered by writing additional mass action expressions and including the competing ions in the mass balance on the surface sites.

Summary

Step 1: Insert a 1 in the first column of line 5 to indicate the type of adsorption algorithm used.

Step 2: Enter a new component (990 or 991) to represent the adsorbing solid and enter a mass for the adsorbing solid.

Step 3: Create the adsorption data base by entering an ID number for the complex formed by the adsorbing species and a log K and stoichiometry for the reaction.

Use of the Freundlich Adsorption Algorithm

The Freundlich adsorption algorithm allows a decrease in the energy of adsorption as the fraction of surface sites covered increases. The decrease in the energy of adsorption with increasing surface coverage is explained by surface heterogeneity. The Freundlich equation also assumes an infinite number of adsorption sites, as does the Kd adsorption algorithm.

The same procedures used to generate an input file for the activity Kd and Langmuir algorithms are also used for the activity Freundlich algorithm. Similar to the other activity adsorption algorithms, a 1 should be inserted in the first column of line 5 in Step 1.

A component is entered in step 2 (e.g., 990) to represent the adsorbing solid. The mass of this component is entered as zero. The activity of the solid need not be entered or a 1.00 may be entered to remind you of the infinite supply of surface sites. The activity doesn't need to be entered because of the type of adsorption algorithm used. The activity of the solid is automatically fixed by the program at 1.00. The activity is fixed at 1.00 because there are an infinite number of adsorption sites.

The component representing the adsorbent is entered as a Type 3 species in step 3 because of the infinite number of adsorption sites.

In step 4, create the adsorption data base by entering an ID number for each reaction, a log K for the reaction, and the stoichiometry for the reaction. The creation of the Freundlich adsorption data base is explained in the following paragraphs.

The equation that describes the mass action expression for the activity Freundlich algorithm is

$$\mathrm{SOH} + (1/n)\ \mathrm{M}^{m+} = \mathrm{SOH\text{-}M}^{m+} \tag{9.11}$$

rearranging Equation (9.1) we end up with the conventional formulation for the Freundlich equation, which is expressed as follows:

$$\mathrm{SOH\text{-}M}^{m+} = K_F(\mathrm{M}^{m+})^{1/n} \tag{9.12}$$

where the activity of SOH is equal to 1, and K_F is the Freundlich activity constant.

To calculate the activity K_F, MINTEQ must be run with the composition of the solution resulting from the experiment used to determine K_F or with an educated guess as to the activity of the adsorbing species. The activity Freundlich is calculated by using the total concentration of the adsorbate (SLD_c) on the solid and the activity of the particular form of the species of interest in solution (A_{as}). A plot of the log of the adsorbed species under consideration (SLD_c) versus the log of the activity of the particular form of the adsorbing species (A_{as}) will give a straight line with a slope of 1/n and

067

an intercept of K_F, if the data conform to the Freundlich. The log of K_F (e.g., 1.5) is entered in the input file, as shown in sample input No. 12.

An additional parameter must be entered in the adsorption species reactions when using the activity Freundlich algorithm because of the difference in reaction stoichiometries between the mass action and mass balance equations. The stoichiometry of the adsorbing species in the mass action expression is 1/n, and the stoichiometry of the same species in the mass balance equation is 1. The mass action stoichiometry [n in Equation (9.11)] for our example (sample problem No. 12) is set to 0.250 for Ca (ID No. 150) in Line 2 of the data base for the Type 2 species. The mass balance stoichiometry is set equal to 1 in the last line of the data base. The 1 in the mass balance stoichiometry indicates that each adsorbing species occupies one adsorption site. You are now ready to run the MINTEQ code and model the system using the activity Freundlich algorithm. If n is equal to 1, then the Freundlich isotherm behaves like the Kd adsorption isotherm.

Summary

Step 1: Enter a 1 in the first column of line 5 to indicate that you are going to use an activity adsorption algorithm.

Step 2: Enter a new component (970 or 991) to represent the adsorbing solid in the Type 2 species.

Step 3: Enter the component chosen for the adsorbing solid (adsorbent) as a Type 3 species (infinite solid)

Step 4: Create the adsorption data base by entering a minimum of an ID number for the complex formed by the adsorbing species, a log K for the adsorption reaction, and the stoichiometry for the reaction.

Use of the Ion Exchange Algorithm

The ion exchange algorithm may be useful if selectivity coefficients for the appropriate exchangeable ions are known. However, the usefulness of the ion exchange algorithm is limited because, usually, selectivity coefficients are known only for macroconstituents of a solution (e.g., sodium, magnesium, potassium, and calcium). Selectivity coefficients for trace metals are rarely obtainable. Additionally, many heavy metals form complexes with adsorbent surface sites and are, therefore, generally unpredictable using exchange mechanisms. The exchange equation, as written in MINTEQ, requires that the activity ratio of the competing ions remains constant even if the concentrations of the competing ions in solution change.

Sample Input No. 12

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EXAMPLE OF ADSORPTION USING THE FREUNDLICH ADSORPTION ALGORITHM.
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
1   0.00   0.00   0.00   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    990 0.000E+00   0.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   4
    330 8.01
    001 7.43
2812800
    990

  2   2
9901400 K-SOH1           0.000     1.500
0.00  2   1.000 410   1.000 990

9901500 CA-SOH1+         0.00      1.500                1.00
0.00  2   0.250 150   1.000 990
                                    1   1.   150
```

Again, as with the activity Kd, Langmuir, and Freundlich isotherms begin step 1 by putting a 1 in the first column of Line 5 to indicate the type of adsorption algorithm you are going to use (sample input No. 13). Then enter a component in the Type 2 data files for step 2. The component ID number will be 995. The concentration of the adsorbent is entered immediately following the ID (995) specification. The concentration of the adsorbent is entered in moles/kg of solution. The log of the activity guess of the adsorbent is entered immediately following the mass. In the third step, enter the adsorbent as a Type 6 species.

The fourth and final step involves the creation of the adsorption data base. To model ion exchange, begin with the exchanger (adsorbent) saturated with one of the ions. The first three lines of the data base [following the Type 6 declaration and after entering the Type 2 declaration and the number of reactions (4); see sample input No. 13] indicate that we are saturating the exchange site with sodium. This is a hypothetical construct done for the purpose of formulating the reaction. The mass balance stoichiometry on the third line signifies that each exchange site is occupied by one sodium ion. There is, however, no mass balance on this exchanger sodium. The following three reactions signify that calcium, magnesium, and potassium, respectively (sample input No. 13), are entering into exchange reactions with the sodium initially present on the exchange sites. The 0.500 in the mass action stoichiometry for the reactions involving magnesium and calcium means that each magnesium and each calcium ion will occupy two exchange sites and displace two sodium ions from those exchange sites. The 0.00 in the third line of each reacting species denotes that there is no mass balance on the sodium that is kicked off the exchange sites by the other exchangers. Therefore, the total aqueous-plus, adsorbed sodium at the end of the run will be equal to the total sodium initially present in the input file. The reactions that we are defining are shown below with potassium representing the other exchangeable ions.

$$K^+ + NaS \rightleftarrows Na^+ + KS \qquad (9.13)$$

where S is the solid phase exchanger (SOH), and NaS is the exchanger initially present that is saturated with sodium. The equilibrium constant (Keq) for this reaction is

$$\frac{[Na+]\ KS}{[K+]\ NaS} = Keq \qquad (9.14)$$

The selectivity or activity exchange coefficient (K'ex) is written as

$$K'eq = \frac{Keq\ NaS}{KS} = \frac{(Na^+)}{(K^+)} \qquad (9.15)$$

Sample Input No. 13

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EXAMPLE OF THE ION EXCHANGE ALGORITHM.
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
1   0.00   0.00   0.00   0.00
    500 1.200E+02  -3.3
    410 1.400E+01  -4.47
    150 1.220E+02  -3.61
    460 7.500E+01  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 1.900E+02  -3.58
    732 2.700E+02  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    995 0.100E-01  -1.80
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   3
    330 8.01
    001 7.43
2812800
  6   1
    995

  2   4
955000  NAX             0.000      0.000
00  1   1.000 995
                                     2   1.   500    1.   995
9951500 CAX              0.00      -0.170                0.00
0.00  3   0.500 150   1.000 995   -1.000 500
                                     1   0.00 500
9954600 MGX              0.000     -0.480
0.00  3   0.500 460   1.000 995   -1.000 500
                                     1   0.00 500
9954100 KX               0.000      0.930
0.00  3   1.000 410   1.000 995   -1.000 500
                                     1   0.00 500
```

This formulation of the exchange equation requires that the solid phase composition (i.e., NaS/KS) remains fixed. This formulation also assumes that there is an infinite reservoir of exchange; thus, the concentration of exchangeables on the surface is much greater than the concentration of the exchangeable ions in solution. Even if the concentrations of the competing exchangeable ions in the solution contacting the exchanger fluctuate, the activity ratio of the competing ions will remain constant because of the large excess of competing ions on the exchanger.

Summary

Step 1: Enter a 1 in the first column of line 5 to indicate the adsorption algorithm used.

Step 2: Enter a new component (995) to represent the adsorbing solid.

Step 3: Enter the new component (adsorbing solid) as a Type 6 species.

Step 4: Create the adsorption data base by entering a minimum of an ID number for the adsorption complex, the log K for the reaction, and the stoichiometry for the reaction.

Surface Complexation Models of Adsorption

Surface complexation models, such as the constant capacitance model and the TLM, were applied with considerable success to single and mixed oxide systems. Surface complexation models of adsorption were originally developed for and applied to crystalline oxides but were successfully applied to amorphous iron oxyhydroxides. Additionally, these surface complexation approaches to adsorption are being tested on heterogeneous solids, such as clays and sediments. If the pH or ionic strength of a modeled system changes significantly, an adsorption approach employing the constant capacitance or the TLM models may give better results than the other adsorption models discussed previously. The effects of surface charge and solution chemistry are incorporated into surface complexation computations and ignored by the models discussed previously. For systems where the concentration of the background electrolyte and the adsorbing species (e.g., metal) remain relatively constant, the constant capacitance model will require fewer experimental parameters than the TLM. If the concentration of the adsorbing species changes, new adsorption constants must be developed for each of the new concentrations. Thus, in applications where the concentration of the adsorbing species varies, the constant capacitance model would require more experimental data than the TLM.

In the surface complexation models, an oxide surface in contact with H_2O is treated as a hydroxylated surface that is represented by SOH, where S is the

0/2

structural metal oxide (e.g., silicon, iron, titanium, aluminum, and manganese). The surface group, SOH, is treated as a ligand in solution and can form complexes with the background electrolyte, metal ions, and other ions in solution analogous to aqueous complexation reactions. There is, however, a fundamental difference between surface complexation or adsorption reactions and complexation reactions taking place in solution. In the surface complexation reactions, a variable electrostatic interaction energy exists between the charged adsorbing species and the charged solid surface. The surface becomes charged because of surface acidity reactions that either protonate or deprotonate the solid surface.

The activities of background and electrolyte ions near the solid surface are different from the concentrations of the same ions in the bulk electrolyte because of the electrostatic potential produced by the surface charge. This electrostatic potential that develops near the surface modifies the activities of the ions near the surface of the solid. The activities near the surface can then be related to the corresponding activities in solution by the Boltzman factor that contains the electrostatic potential as a term. The Boltzman factor is treated as just another component in the MINTEQ code.

There are basic differences between the constant capacitance model of adsorption and the triple-layer model of adsorption. One of the differences concerns the ions that are allowed to adsorb, and where these ions are allowed to adsorb. The constant capacitance model does not consider the adsorption of the background electrolyte, while the triple-layer model allows background electrolyte adsorption to occur. Also, the triple-layer model allows only protonation and deprotonation reactions at the solid surface, while in the constant capacitance model, specifically adsorbed ions adsorb at the surface, in addition to the protonation and deprotonation reactions that occur.

Using the Constant Capacitance Model of Adsorption

In the constant capacitance model, all specifically adsorbed ions (H^+, OH^-, and M^{n+}, where M^{n+} represents a metal ion) compete for the same surface sites and are adsorbed in the surface plane [(o plane) Figure 9.1]. Ions that are not specifically adsorbed are considered to be located in the diffuse layer. The total surface charge is set by the charges of the adsorbed ions and will determine the surface potential. The dominant contribution to the surface charge (s_0) is from the potential determining hydronium and hydroxyl ions. The surface potential will, in turn, affect the activities of the adsorbing species at the solid surface. Activity coefficients for all surface species are set equal to 1. As mentioned, the activities of the adsorbing species at the solid surface will be different from what they were in solution. The activities of the surface species are set equal to concentrations and then computed by an exponential Boltzman factor.

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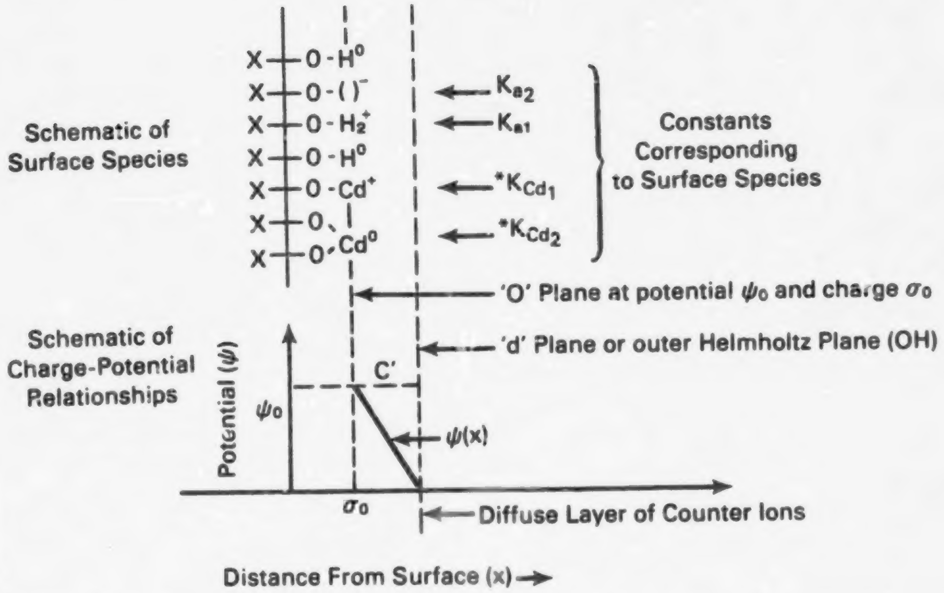
Schematic of Surface Species
X—O-H⁰
X—O-( )⁻
X—O-H₂⁺
X—O-H⁰
X—O-Cd⁺
X—O
X—O Cd⁰
Kₐ₂
Kₐ₁
*K_Cd1
*K_Cd2
Constants Corresponding to Surface Species
'O' Plane at potential ψ₀ and charge σ₀
'd' Plane or outer Helmholtz Plane (OH)
Schematic of Charge-Potential Relationships
Potential (ψ)
ψ₀
C'
ψ(x)
σ₀
Diffuse Layer of Counter Ions
Distance From Surface (x)

FIGURE 9.1. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Constant Capacitance Layer Model. Brackets in the "zero" plane indicate deprotonated surface sites.

The complexation of background electrolytes with surface sites is ignored in the constant capacitance model. The capacitance term and the adsorption constants are dependent on the type and concentrations of the background electrolyte and are only good for the specific electrolytes and concentrations in which the adsorption data were obtained. Figure 9.1, taken from Felmy et al. (1984), is a schematic of the constant capacitance or electric double-layer model of adsorption.

The required MINTEQ input data for the constant capacitance model of adsorption are 1) an inner layer capacitance (C1) expressed in Farads/m^2, 2) the electrostatic potential (E_0) in volts, 3) the concentration of the adsorbent (SOH) given in g/L, 4) the specific surface area (SSA) expressed in m^2/g, 5) the surface site density (sites/m^2), and 6) the equilibrium mass action expressions for adsorption with the corresponding equilibria constants.

The concentration and surface area of the adsorbent and the inner layer capacitance must all be entered in Step 1. The steps and changes are again indicated by arrows on the input files. It is not necessary to make any changes to Lines 1-4 to use the surface complexation models of adsorption. In step 1, enter a "2" in the first column of Line 5 to indicate that you are going to use the constant capacitance model of adsorption. In the next format field on Line 5, enter the concentration of the adsorbent in g/L. For the third parameter on Line 5, enter the surface area of the adsorbent in m^2/g. For the last required input on this line, enter the inner layer capacitance in Farads/m^2. The value of the inner-layer capacitance is usually about 1.4 Farads/m^2.

Next, in step 2, add two new components to the the Type 1 species under the ID No. 990 and 992, as shown in sample input No. 14. The adsorbent is represented by the component 990. In place of a mass for the adsorbent, enter the total number of adsorption sites per gram of adsorbent. The component ID No. 992 represents the electrostatic potential in the surface plane. The component name for the electrostatic potential of the surface plane is XPSIO. No mass is entered for the surface potential, while the activity of the surface potential is entered as the log of the dimensionless potential. The log value of XPSIO will generally range from -0.2 to -4.0. We entered a -3.0 for this potential in sample input No. 14.

The next modification (step 3) for using the constant capacitance model is in the Type 6 species. The electrostatic potential of the surface plane (992) is entered as a Type 6 species because it has no mass.

The final step (step 4) is entering the mass action expressions for each of the adsorption reactions as Type 2 species. The format is the same as those used previously to insert species (see Generalized Data File Format). The ID number of the entered complex should begin with 990 followed by the ID number of the adsorbing species. Continuing on the first line, enter the name of your complex, and the log K of the adsorption reaction. On the second line of the thermodynamic data for the Type 2 species, enter the components involved in the reaction. The only major difference between previous adsorption algorithms discussed and the constant capacitance algorithm is that one of the components (ID 992) is the electrostatic potential in the "o" plane, or plane of specific adsorption. The 1.0 entered for the stoichiometry of the electrostatic component (XPSIO, 992) in sample input No. 14 is computed from a summation of the stoichiometric coefficients of the electrostatic components for the hydronium ion and for the calcium ion. The electrostatic stoichiometric coefficient for the calcium ion is +2, because it is on the left side (according to the convention used in MINTEQ) of the reaction and has a +2 charge. However, the electrostatic stoichiometric coefficient for the hydronium ion is a -1.0, because it is singly charged and located on the right side of the reaction. The summation of these two stoichiometric coefficients equals a +1.0; this is further

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Sample Input No. 14

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
EXAMPLE OF ADSORPTION USING CONSTANT CAPACITANCE MODEL.
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
2   2.67 600.00   1.40   0.00
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    990 5.880E+21   0.00
    992 0.000E+00  -3.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   3
    330 8.01
    001 7.43
2812800
  6   1
    992

  2   1
9901500 SO-CA+            0.00     -6.20                  1.00
0.00  4   1.000 150   1.000 990  -1.000 330   1.000 992
```

illustrated by the reactions given below where Ca^{2+} is permitted to adsorb onto the surface of a metal oxide by the constant capacitance model.

$$SOH + Ca^{2+} = [SO^{-}\text{--}Ca^{2+}]^{+} + H^{+}_{s} \tag{9.16}$$

where SOH is the metal oxide surface, $[SO^{-}\text{--}Ca^{2+}]^{+}$ is the surface complex formed by the adsorbing calcium, and the subscript s indicates that the hydronium is in the electrostatic double layer, instead of in the bulk solution. The equilibrium expression for this adsorption reaction is

$$^{*}Kd_{Ca} = \frac{[SO^{-}\text{--}Ca^{2+}]^{+}\ [H^{+}_{s}]\ \exp\ (-x\psi_{o})}{[SOH]\ [Ca^{2+}]\ \exp\ (-2x\psi_{o})} \tag{9.17}$$

where x = F/RT
F = the Faraday's constant
R = the gas constant in Joules
T = the absolute temperature
ψ_{o} = the electrostatic potential at the "o" or surface plane
exp(x) = exponential function where $f(x) = e^{(x)}$

The hydronium and calcium ions are both in the electrostatic double layer and have potentials ψ_{o}. As explained previously, adding the +2 and -1 (because the potentials are on the reactant and product sides of the reaction, respectively) gives a net ψ_{o} of +1. The electrostatic component is treated like any other component. In sample input No. 14, the above reaction is coded into the Type 2 or thermodynamic data file. The asterisk (*) indicates that the adsorption constant used in MINTEQ is not the intrinsic constant referred to in much of the experimental literature (Davis et al. 1978; Davis and Leckie 1978; Davis and Leckie 1980). The adsorption constant in MINTEQ is written in terms of the neutral surface site (SOH). Intrinsic constants are written in terms of protonated (SOH_{2}^{+}) and deprotonated (SO^{-}) surface sites. You must also remember to insert "log *K" and not "*K" when inputting this information into the file. In Sample Input No. 14, the constant used in MINTEQ (log *K) is the sum of the log of the intrinsic constant for Ca^{2+} (4.5) and the log of the second acidity constant (-10.7) for the amorphous iron oxide. Further details on the construction of the input for the thermodynamic data for Type 2 species are given in the following section on the triple-layer model of adsorption.

Summary

Step 1: Insert a 2 in the first column at line 5 to indicate you are using the constant capacitance model of adsorption. Also, on line 5, enter the concentration of the adsorbent, the surface area of the adsorbent, and the inner layer capacitance.

Step 2: Enter two new components into the Type 2 species. One component (e.g., 990) is used to represent the solid, and another component (992) represents the electrostatic potential in the surface plane.

Step 3: Enter the electrostatic component (992) as a Type 6 species.

Step 4: Create the adsorption data base as explained in the text.

Using the Triple-Layer Model of Adsorption

The Triple-Layer Model of adsorption considers the adsorption layer to be composed of two constant capacitance layers bounded by a diffuse layer of electrolytes. The hydronium and hydroxyl ions are the only ions adsorbed in the inner layer ("o" plane). The hydronium and hydroxyl ions contribute to the surface charge (s_0) and are subject to the surface potential ψ_0. Specifically adsorbed and background electrolyte ions are adsorbed in the inner Helmholtz layer ("b" plane) and affect the charge in this layer (s_b). These ions also respond to the potential ψ_b. The outer Helmholz layer ("d" plane) is the inner boundary of nonspecifically adsorbed ions (see Figure 9.2). Nonspecifically adsorbed ions contribute to the charge s_d and are influenced by the potential ψ_d. These three electrostatic potentials must be included when using the TLM.

Step 1 in using the TLM model of adsorption is basically the same as step 1 in using the constant capacitance model of adsorption. As mentioned, there is no need to change Lines 1-4 to use either of the surface complexation algorithms. To indicate that you are using the TLM adsorption algorithm, a "3" must be entered in Column 1 of Line 5. The next three inputs are the same as the inputs for the constant capacitance model. Enter, on the same line, the concentration of the adsorbent in g/L, the surface area of the adsorbent in m^2/g, and the inner layer capacitance in Farads/m^2. Because an additional capacitance term is needed for the TLM adsorption algorithm, you must also enter a value for the outer layer capacitance [(C2) (Farads/m^2)] in the fifth format field of Line 5. The value of the outer layer capacitance is generally around 0.20 Farads/m^2. Sample input No. 15 is an input file for the TLM adsorption algorithm.

In step 2, four components are added to the component (Type 1) input file. The added components have ID Nos. 990, 992, 993, and 994. As indicated previously, the component with ID No. 990 represents the adsorbent (SOH). The number of sites/g for the adsorbent (990) is entered where the component mass is normally placed. The number of sites/g (5.88×10^{21}) was calculated using a

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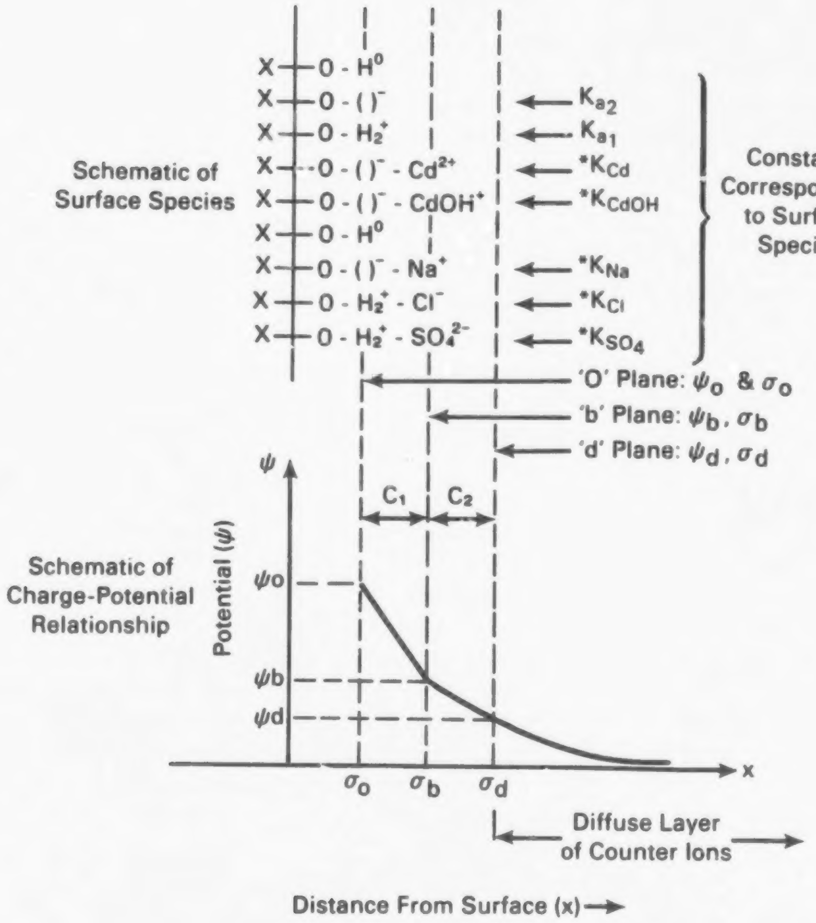
Schematic of Surface Species
X—O - H^0
X—O - ( )$^-$
X—O - H_2^+
X—O - ( )$^-$ - Cd^{2+}
X—O - ( )$^-$ - $CdOH^+$
X—O - H^0
X—O - ( )$^-$ - Na^+
X—O - H_2^+ - Cl^-
X—O - H_2^+ - SO_4^{2-}
K_{a_2}
K_{a_1}
$^*K_{Cd}$
$^*K_{CdOH}$
$^*K_{Na}$
$^*K_{Cl}$
$^*K_{SO_4}$
Constants Corresponding to Surface Species
'O' Plane: ψ_o & σ_o
'b' Plane: ψ_b, σ_b
'd' Plane: ψ_d, σ_d
ψ
C_1
C_2
Schematic of Charge-Potential Relationship
Potential (ψ)
ψo
ψb
ψd
x
σ_o
σ_b
σ_d
Diffuse Layer of Counter Ions
Distance From Surface (x)

FIGURE 9.2. Schematic Representation of Surface Species and Surface Charge-Potential Relationship for the Triple Layer Model. Brackets in the "zero" plane indicate deprotonated surface sites.

value of 9.8 sites/nm^2 and a surface area of 600 m^2/g. The ID Nos. 992, 993, and 994 designate the electrostatic potentials for the surface plane ("o" plane), inner Helmholz layer ("b" plane), and the the inner diffuse layer plane ("d" plane), respectively. Guesses between -0.2 to -0.4 for the log of the activity are appropriate for these electrostatic potentials. The component names for the electrostatic potentials are XPSIO, XPSIB, and XPSID and the corresponding ID Nos. are 992, 993, and 994, respectively.

In step 3, components 992, 993, and 994 must also be entered as Type 6 species (see sample input No. 15).

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Sample Input No. 15

```
MODIFIED RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979)
EXAMPLE OF ADSORPTION USING TRIPLE-LAYER MODEL
9.5 'MG/L' 0.00
0 0 0 0 2 0 0 0 0
3   2.47    600.   1.40   0.20
    500 1.200E+01  -3.3
    410 1.400E+00  -4.47
    150 1.220E+01  -3.61
    460 7.500E+00  -3.60
    770 2.913E+01  -3.52
    140 7.397E+01  -5.66
    180 9.900E+00  -3.58
    732 7.700E+00  -4.21
    280 1.500E-02 -11.45
    281 7.000E-04 -17.45
    990 5.880E+21   0.00
    992 0.000E+00  -3.00
    993 0.000E+00  -4.00
    994 0.000E+00  -4.00
    001 0.000E+00  -7.43
    330 0.000E+00  -8.01

  3   3
    330 8.01
    001 7.43
2812800
  6   3
    992
    993
    994

  2   7
9903300 SO-                      -10.70
      3   1.0   990  -1.0   330  -1.0   992

9903301 SOH2+                      5.10
      3   1.    990   1.    330   1.    992

9905000 SO-NA                    -9.00
      5   1.    990   1.    500  1.     993  -1.    330  -1.     992

9901500 SO-CA+                   -6.2                 1.00
      5   1.    990   1.    150  2.     993  -1.    330  -1.     992

9901501 SO-CAOH                 -15.6
      6   1.    990   1.    150  1.     993  -2.    330  -1.     992   1.    002

9907320 SOH2-SO4-                 9.9                -1.00
      5   1.    990   1.    732  1.     992   1.    330  -2.     993
                                    1   3.   990
9907321 SOH2-HSO4                15.9
      5   1.    990   1.    732  1.     992   2.    330  -1.     993
                                    1   3.   990
```

The final step (step 4) is to formulate the mass action expressions for the adsorption reactions. The inclusion of surface electrolyte reactions and the multiple-layer structure of the interface permit the adsorption constants for the TLM to be applicable over a wide range of pH values and electrolyte and adsorbate concentrations. However, experimental data over a wide range of conditions are necessary to determine these constants.

As discussed previously, MINTEQ requires that the log *K constants be written in terms of the neutral surface site (SOH). Values in the literature may be written in terms of intrinsic constants (K^{int}) (i.e., in terms of the protonated surface site (SOH_2^+) for adsorbing anions and deprotonated surface sites (SO^-) for adsorbing cations). Formulae for converting intrinsic constants found in the literature to the constants used in MINTEQ (*K) are given below.

$$\log {}^*K_{anion} = \log K_{a1}^{int} + \log K_{anion}^{int} \qquad (9.18)$$

$$\log {}^*k_{\substack{hydrated\\anion}} = \log K_{a1}^{int} + \log K_{\substack{hydrolysis\ of\\anion}} + \log K^{int}{}_{\substack{hydrated\\anion}} \qquad (9.19)$$

$$\log {}^*K_{cation} = \log K_{cation}^{int} + \log K_{a2}^{int} \qquad (9.20)$$

$$\log {}^*K_{\substack{hydrated\\cation}} = \log K_{a2}^{int} + \log K^{int}_{\substack{hydrated\\cation}} + \log K_{\substack{hydrolysis\ of\\cation}} \qquad (9.21)$$

where int is the intrinsic constant, and a1 and a2 are the first and second acidity constants for the surface site. The log Ks for the hydrolysis species are for reactions written as formation reactions. For amorphous iron oxyhydroxide, the reactions for the first and second acidity constants are, respectively,

$$SOH + H_s^+ = SOH_2^+$$

with an equilibrium expression of

$$K_{a1}^{int} = \frac{[SOH_2^+]}{[SOH]\,[H_s^+]} = 10^{+5.1} \qquad (9.22)$$

and

$$SOH = SO^- + H_s^+$$

where the equilibrium expression for the second acidity constant is

$$K_{a2}^{int} = \frac{[SO^-]\,[H_s^+]}{[SOH]} = 10^{-10.7} \qquad (9.23)$$

The creation of input files for the adsorption of cations, anions, and hydrolyzed species is explained in the following discussion. The input for the following reactions is illustrated in sample input No. 15. The adsorption of divalent calcium can be written as

$$SOH + Ca_s^{2+} = [SO^- \text{--} Ca^{2+}]^+ + H_s^+$$

where the equilibrium expression is

$$^*K = \frac{[SO^- \text{--}\; Ca^{2+}]^+\,[H_s^+]\,\exp\,(-x\psi_o)}{[SOH]\,[Ca_s^{2+}]\,[\exp\,(-2x\psi_b)]} \qquad (9.24)$$

The electrostatic potential in the "o" plane (ID 992) has a stoichiometric coefficient of -1.0, because the hydronium cation is singly charged and on the product side of the reaction. The stoichiometric coefficient of the electrostatic potential in the "b" plane (993) is +2.0, because the calcium cation has a charge of +2.0 and is on the reactant side of the reaction. Remember that the formulation of reactions in MINTEQ reactants have positive stoichiometric coefficients, and products (right side of reaction) have negative stoichiometric coefficients. The coefficients for the other components are based on mass action expressions for the adsorption reactions. In this discussion, we will only talk about the coefficients for the electrostatic potentials. The log *K was determined by summing the log Ks for the second acidity reaction (-10.7) of the solid surface and the intrinsic constant (4.5) for divalent calcium.

As another example, the adsorption of hydrolyzed calcium may be written as

$$SOH + Ca_s^{2+} + H_2O = [SO^- - CaOH^+] + 2H_s^+ \qquad (9.25)$$

$$\text{and } ^{*}K = \frac{[SO^{-} - Ca^{2+}]\,[H^{+}_{s}]^{2} \exp(-x\psi_{o}) \exp(-x\psi_{b})}{[SOH]\,[Ca^{2+}_{s}] \exp(-2x\psi_{b})\,[H_{2}O]} \qquad (9.26)$$

Here, the calculation of the potential for the "o" plane (992) is straightforward having a coefficient of -1.0. To obtain the coefficient for the "b" plane (993), you must add a -1.0 for one of the hydronium ions and a +2.0 for the calcium ion to obtain a net +1.0 for the coefficient. One of the hydronium ions is kicked off the surface plane affecting the potential ψ_o, while the other hydronium in the "b" plane from the hydrolysis of calcium is contributing to the potential ψ_b. The log *K for the sorption of the hydrolyzed calcium was obtained by summing the following equations:

$$SOH = SO^{-} + H^{+}_{s} \qquad K^{int}_{a2} \qquad (9.27)$$

$$SO^{-} + CaOH^{+} = SO^{-} - CaOH+ \qquad K^{int}{}_{CaOH} \qquad (9.28)$$

$$Ca^{2+} + H_{2}O = CaOH^{+} + H^{+}_{s} \qquad K_{\text{Hydrolosis of cation}} \qquad (9.29)$$

The log Ks for the above reactions are -10.7, 7.7, and -12.6, respectively. Adding together these three reactions gives reaction No. 9.25 and a log *K of -15.6 (see sample input No. 15) for this reaction.

The final example involves the adsorption of a divalent anion, as shown in equation No. 19.30.

$$SOH + H^{+}_{s} + SO^{2-}_{4s} = [SOH^{+}_{2} - SO^{2-}_{4}]^{-} \qquad (9.30)$$

where the equilibrium expression is

$$^{*}K = \frac{[SOH^{+}_{2} - SO^{2-}_{4}]^{-}}{[SOH]\,[H^{+}_{s}] \exp(-x\psi_{o})\,[SO^{2-}_{4}] \exp(+2x\psi_{o})} \qquad (9.31)$$

The stoichiometric coefficient for the electrostatic term in the "o" plane is +1 because the hydronium ion is positively charged and situated on the reactant side of the equation. The electrostatic potential in the "b" plane has a coefficient of -2.0 (see sample input No. 15). The negative charge on the sulfate changes the sign of the coefficient and the 2 comes from the magnitude of the

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charge on the sulfate ion. The log *K comes from the addition of the first surface acidity constant and the intrinsic constant for the sulfate anion.

The stoichiometry for the mass action expression is different from the stoichiometry for the mass balance expression for the adsorption of sulfate. Line 3 of the thermodynamic input for the sulfate (and bisulfate) ion contains information for the mass balance expression. The 3 indicates that every sulfate ion occupies three adsorption sites. The number of sites that each ion occupies may be found in the literature and is determined experimentally.

CHAPTER 10

ERROR MESSAGES

The MINTEQ computer code was designed to identify a limited number of common error situations that can occur during execution. It should be kept in mind, however, that not all run-time errors are trapped by the MINTEQ code, and system run-time diagnostics can occur under certain situations. The subroutine ERROR is used to print out error messages for twelve error conditions. In addition, the problem data are printed at the time an error occurs to aid in identifying the cause of the error and the possible corrective action.

ERROR 1. COMPONENTS > NXDIM

This error condition is generated by subroutine INPUT if the number of components specified is greater than the dimensioned array size. The total number of components in the problem must be less than or equal to forty in the current version of MINTEQ. This total includes the components that MINTEQ automatically enters [i.e., H_2O and S(0) for polysulfide calculations]. If no components can be eliminated from the conceptual model, the array sizes in COMMON.DAT, and the variable NXDIM in subroutine MAIN must be changed and the program recompiled.

ERROR 2. SPECIES > NYDIM

This error condition is generated by subroutine INPUT if the number of species in the problem is greater than the dimensioned array size. The total number of species must be less than or equal to 550 in the current version of MINTEQ. The total number of species is the sum of the Type 1, Type 2, Type 3, Type 4, Type 5, and Type 6 species. This error can occur if all of the solids in the data base are included as Type 5 species. If the conceptual model cannot be reduced in size, the array sizes in COMMON.DAT and the variable NYDIM in subroutine MAIN must be changed and the program recompiled.

ERROR 3. SPECIES NOT FOUND

This error condition is generated by subroutine INPUT if species ID numbers specified in SAMPLE.DAT are not found in the data base. This error condition can result from entering an incorrect ID number or entering the ID number in the incorrect format field.

ERROR 4. CHARGE BALANCE > 30%

This error condition is generated by subroutine PREP if the initial (i.e., analytic) charge balance difference is greater than 30%. This error condition can be circumvented by setting the charge balance termination option to 1. The error condition is caused by an inaccurate or incomplete set of component analytic molalities.

ERROR 5. INPUT TYPE > 6

This error condition is generated by subroutine INPUT if a species type greater than 6 was present in SAMPLE.DAT. The condition is generated by a typographical error in the input file.

ERROR 6. PHASE RULE VIOLATION

This error condition is generated by either subroutine SOLID or subroutine SOLVE. The error condition occurs if the number of degrees of freedom in the problem is reduced below one. The cause of this error condition is the specification of more activity constraints (defined by Type 3 and Type 4 species) than independent components. The error can arise as the result of an incorrect conceptual model or as the result of MINTEQ attempting to find the stable equilibrium assemblage. A phase rule violation can only be corrected by changing the conceptual model, specifically, the Type 3, Type 4, and Type 5 species.

ERROR 7. ITERATIONS > ITMAX

This error condition is generated by subroutine SOLVE when the number of iterations needed to solve the problem exceeds the maximum number of iterations specified. The specified number of iterations is set by the total iterations option to 40, 10, 100, or 200 iterations. (It should be kept in mind that the total number of iterations is cumulative as solids enter and leave the assumed stable phase assemblage.) This error condition was designed to place a limit on the amount of computer time that would be wasted if true nonconvergence occurs. Nonconvergence in the Newton-Raphson algorithm can be caused by poor initial activity guesses. Specification of accurate guesses is required to solve some problems, particularly when strongly complexing and/or polynuclear species are in the problem.

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ERROR 8. SINGULAR Z MATRIX

This error condition is generated by subroutine SIMQ when the Jacobian matrix has a zero determinant. The error condition is caused by an error in the conceptual model when the set of components does not span the species space. In particular, some subset of the components are not linearly independent. This condition can only be corrected by changing the conceptual model.

ERROR 9. INVALID COMPONENT

This error condition is generated by subroutine INPUT when a component ID number in SAMPLE.DAT could not be found in the component data base. This error condition is commonly the result of a typographical error in the input file.

ERROR 10. NOT ENOUGH ADS PARAMETER

This error condition is generated by subroutine INPUT when the adsorption data input in SAMPLE.DAT is insufficient. This error condition is the result of a typographical error in the input file.

ERROR 11. A COMPONENT X = 0.0

This error condition is generated by either subroutine CONVG or by subroutine SOLVE. The error condition results when the activity of one of the components is equal to zero. This error condition is the result of an incorrect conceptual model and arises in the first Newton-Raphson iteration. The error condition can be corrected by removing the offending component or by providing an improved activity guess for the component. The error may also arise if both components in a redox couple are specified, one with zero mass. The redox couple was not made a Type 3 species.

ERROR 12. AN X APPROACHES ZERO

This error condition is generated by subroutine SOLVE when the activity of a component is approaching zero. This error condition arises during the Newton-Raphson iteration when a component activity must tend to zero to satisfy the mass balance equations. This error condition is not generally the result of an incorrect conceptual model, as is error 11. A different activity guess, or a change in the conceptual model to remove the offending component can correct this error.

CHAPTER 11

OUTPUT

After running the MINTEQ computer code, you must be able to interpret the output to receive any benefit from the modeling efforts. In this section, we will explain the output from a selected MINTEQ run using the output from sample input No. 7 as our example. This example was chosen because it considers ion speciation/solubility and mass transfer calculations. The entire output file will not be replicated for the following discussion, only portions will be extracted to represent the various parts of the output file. The output is presented in sample output Nos. 1-11.

The first part of the output file (sample output No. 1) contains the input file. Thus, the first part of sample output No. 1 is identical to sample input No. 7, except that MINTEQ inserted the message "$H2_0$ HAS BEEN INSERTED AS A COMPONENT" into the output file; this reflects the fact that MINTEQ automatically inserts the H_2O component into the input file on every run.

The second part of the output file contains information on the unspeciated charge balance. The sum of the equivalents of the anions and cations is given along with the percent difference between the two as calculated by the equation that is shown (sample output No. 2).

The third part of the output tells us the number of iterations that MINTEQ required to solve the problem outlined in the input file. For our particular problem, MINTEQ required five iterations to speciate the initial input file. When a solid precipitates or dissolves, MINTEQ must go through additional iterations to solve the equilibrium problem with the new solution composition resulting from the precipitation or dissolution process. In this initial speciation, the Type 4 species (solids with a finite mass) are equilibrated with the input solution. In this case (sample input No. 7), because we specified calcium carbonate as a Type 4 species, the calcium carbonate dissolves until it comes to equilibrium with the initial input solution. The speciation of input file No. 7 includes the calcium and carbonate from the calcium carbonate that dissolved. If the solid entered as a Type 4 species is very soluble, large quantities of it may go into solution to equilibrate the solid with the solution. In some of these cases, because of the high ionic strength of the solution resulting from the solid that dissolves, MINTEQ may not converge. If this occurs, it may be necessary to "hand dissolve" the solid (i.e., take the contribution of each component to the total mass of the solid and enter each contribution as a Type 1 component). If you "hand dissolve" the solid, the solid must be changed from a Type 4 to a Type 5 species.

Sample Output No. 1

```
MODEL: MINTEQ  VERSION: EPA 82  RUN ON:  AT

THIS IS THE RIVER WATER TEST CASE PUBLISHED IN NORDSTROM ET AL. (1979).
CONTACTING TYPE 4 AND 5 SOLIDS-ELEMENTS NOT IN DATA BASE ARE EXCLUDED.
 T =    9.50 MG/L    0.00
 0 0 1 0 2 0 0 0 0
 0   0.00   0.00   0.00   0.00
     500  1.200E+01  -3.30
     410  1.400E+00  -4.47
     150  1.220E+01  -3.61
     460  7.500E+00  -3.60
     770  2.913E+01  -3.52
     140  7.397E+01  -5.66
     180  9.900E+00  -3.58
     732  7.700E+00  -4.21
      90  2.860E-01  -5.35
     130  6.000E-03  -7.15
     380  1.800E-03  -7.87
     270  1.000E-01  -5.31
     580  2.100E-01 -10.35
     492  8.980E-01  -4.77
     491  1.900E-02  -5.32
     490  1.440E-01 -17.71
     280  1.500E-02 -11.45
     281  7.000E-04 -17.45
     470  2.200E-03  -7.19
     471  2.200E-03 -26.30
      30  5.000E-03 -14.84
     950  4.900E-04  -8.41
     160  1.000E-04  -9.32
     600  3.000E-05 -11.46
     230  2.000E-04 -15.25
     231  3.000E-04 -10.47
     540  1.800E-03  -8.76
      20  4.000E-05  -9.68
      60  1.681E-03 -24.97
      61  1.895E-03 -22.00
       1  0.000E+00  -7.84
     330  0.000E+00  -8.01

H2O HAS BEEN INSERTED AS A COMPONENT
   3   8
     330  8.010E+00    0.00
       1  7.840E+00    0.00
 2812800  0.000E+00    0.00
 2302310  0.000E+00    0.00
 4714700  0.000E+00    0.00
 4904920  0.000E+00    0.00
 4914920  0.000E+00    0.00
  600610  0.000E+00    0.00
   4   1
 5015001  0.000E+00    0.00  1.000E-01
   5   3
 2028100  0.000E+00    0.00
 6015001  4.600E+00    0.00
 2077004  0.000E+00    0.00
```

Sample Output No. 2

```
CHARGE BALANCE: UNSPECIATED
     SUM OF CATIONS = 1.793E-03 SUM OF ANIONS = 2.932E-03
     PERCENT DIFFERENCE =  2.410E+01   (ANIONS - CATIONS)/(ANIONS + CATIONS)
```

Sample Output No. 3

```
ITERATIONS DURING SOLVE

       0       ITER       NAME         TOTAL MOL     DIFF FXN     LOG ACTVTY
                  1   NA                5.221E-04  -1.971E-05     -3.30000
                  2   CA               -9.284E-04  -1.567E-03     -3.37137
                  3   NA                5.221E-04   3.325E-05     -3.28269
                  4   NA                5.221E-04   2.089E-06     -3.30944
                  5   MG                3.085E-04   3.363E-07     -3.63084
```

Sample Output No. 4

```
OUTPUT DATA:  ITERATIONS = 5

 ID  NAME     ANAL MOL   CALC MOL    ACTIVITY   LOG ACTVTY    GAMMA    NEW LOGK   DIFF FXN
500  NA      5.221E-04  5.216E-04  4.883E-04    -3.31130   0.936209   0.0286   9.296E-09
410  K       3.581E-05  3.580E-05  3.345E-05    -4.47554   0.934498   0.0294   6.578E-10
150  CA      3.044E-04  9.211E-04  7.136E-04    -3.14653   0.774783   0.1108   3.045E-08
460  MG      3.085E-04  3.009E-04  2.337E-04    -3.63131   0.776829   0.1097   1.942E-08
770  H4SIO4  3.031E-04  3.015E-04  3.017E-04    -3.52036   1.000908  -0.0004  -1.778E-10
600  PB      1.448E-10  1.853E-12  1.421E-12   -11.84744   0.766624   0.1154   5.650E-17
180  CL      2.793E-04  2.793E-04  2.610E-04    -3.58336   0.934498   0.0294   5.090E-09
732  SO4     8.017E-05  7.114E-05  5.448E-05    -4.26373   0.765864   0.1158   5.162E-09
 90  H3BO3   4.626E-06  4.419E-06  4.423E-06    -5.35432   1.000908  -0.0004   1.381E-12
130  BR      7.510E-08  7.510E-08  7.026E-08    -7.15327   0.935572   0.0289   1.270E-12
380  I       1.419E-08  1.418E-08  1.326E-08    -7.87732   0.935719   0.0289   2.578E-13
270  F       5.264E-06  5.189E-06  4.852E-06    -5.31407   0.934977   0.0292   9.513E-11
580  PO4     2.212E-06  6.684E-11  3.711E-11   -10.43045   0.555306   0.2555   1.042E-10
492  NO3     1.448E-05  2.195E-05  2.051E-05    -4.68805   0.934371   0.0295   4.280E-10
230  CU+1    3.148E-09  2.183E-16  2.038E-16   -15.69070   0.933753   0.0298  -2.018E-14
 20  AG      3.709E-10  2.245E-10  2.101E-10    -9.67764   0.935719   0.0289   3.828E-15
280  FE+2    2.686E-07  1.780E-12  1.377E-12   -11.86102   0.773624   0.1115   3.446E-12
540  NI      3.066E-08  9.338E-10  7.159E-10    -9.14516   0.766624   0.1154   1.245E-13
470  MN+2    4.005E-08  7.812E-08  6.043E-08    -7.21871   0.773624   0.1115   5.216E-12
 60  H3ASO3  1.335E-08  1.528E-26  1.530E-26   -25.81536   1.000908  -0.0004   1.811E-12
 30  AL      1.853E-07  2.508E-15  1.451E-15   -14.83845   0.578368   0.2378   7.145E-13
950  ZN      7.497E-09  3.359E-09  2.599E-09    -8.58521   0.773624   0.1115   2.614E-13
160  CD      8.898E-10  4.041E-10  3.098E-10    -9.50895   0.766624   0.1154   2.987E-14
  2  H2O     1.985E-22 -2.524E-05  9.999E-01    -0.00002   1.000000   0.0000   0.000E+00
491  NO2     4.131E-07  9.327E-07  8.727E-07    -6.05913   0.935719   0.0289   0.000E+00
490  NH4     7.984E-06  1.310E-21  1.223E-21   -20.91247   0.933753   0.0298   0.000E+00
281  FE+3    1.254E-08  6.065E-18  3.508E-18   -17.45496   0.578368   0.2378   0.000E+00
231  CU+2    4.722E-09  4.047E-11  3.131E-11   -10.50438   0.773624   0.1115   0.000E+00
471  MN+3    4.005E-08  2.073E-26  1.199E-26   -25.92112   0.578368   0.2378   0.000E+00
  1  E       0.000E+00  6.309E-05  1.445E-08    -7.84000   1.000000   7.8400   0.000E+00
 61  H3ASO4  1.335E-08  1.713E-15  1.715E-15   -14.76580   1.000908  -0.0004   0.000E+00
330  H       0.000E+00 -1.825E-03  9.772E-09    -8.01000   0.940975   8.0100   0.000E+00
140  CO3     1.233E-03  7.147E-06  5.513E-06    -5.25859   0.771430   0.1127   0.000E+00
```

```
                           Sample Output No. 5

SPECIES:   TYPE  I - COMPONENTS

ID   Name         CALC MOL   ACTIVITY   LOG ACTVTY   GAMMA     NEW LOGK     DH
500  NA          5.216E-04  0.0004883   -3.31130   0.936209     0.029     0.000
410  K           3.580E-05  0.0000335   -4.47554   0.934498     0.029     0.000
150  CA          9.211E-04  0.0007136   -3.14653   0.774783     0.111     0.000
460  MG          3.009E-04  0.0002337   -3.63131   0.776829     0.110     0.000
770  H4SIO4      3.015E-04  0.0003017   -3.52036   1.000908     0.000     0.000
140  CO3         7.147E-06  0.0000055   -5.25859   0.771430     0.113     0.000
180  CL          2.793E-04  0.0002610   -3.58336   0.934498     0.029     0.000
732  SO4         7.114E-05  0.0000545   -4.26373   0.765864     0.116     0.000
 90  H3BO3       4.419E-06  0.0000044   -5.35432   1.000908     0.000     0.000
130  BR          7.510E-08  0.0000001   -7.15327   0.935572     0.029     0.000
380  I           1.418E-08  0.0000000   -7.87732   0.935719     0.029     0.000
270  F           5.189E-06  0.0000049   -5.31407   0.934977     0.029     0.000
580  PO4         6.684E-11  0.0000000  -10.43045   0.555306     0.255     0.000
492  NO3         2.195E-05  0.0000205   -4.68805   0.934371     0.029     0.000
491  NO2         9.327E-07  0.0000009   -6.05913   0.935719     0.029     0.000
490  NH4         1.310E-21  0.0000000  -20.91247   0.933753     0.030     0.000
280  FE+2        1.780E-12  0.0000000  -11.86102   0.773624     0.111     0.000
281  FE+3        6.065E-18  0.0000000  -17.45496   0.578368     0.238     0.000
470  MN+2        7.812E-08  0.0000001   -7.21871   0.773624     0.111     0.000
471  MN+3        2.073E-26  0.0000000  -25.92111   0.578368     0.238     0.000
 30  AL          2.508E-15  0.0000000  -14.83845   0.578368     0.238     0.000
950  ZN          3.359E-09  0.0000000   -8.58521   0.773624     0.111     0.000
160  CD          4.041E-10  0.0000000   -9.50895   0.766624     0.115     0.000
600  PB          1.853E-12  0.0000000  -11.84744   0.766624     0.115     0.000
230  CU+1        2.183E-16  0.0000000  -15.69070   0.933753     0.030     0.000
231  CU+2        4.047E-11  0.0000000  -10.50438   0.773624     0.111     0.000
540  NI          9.338E-10  0.0000000   -9.14516   0.766624     0.115     0.000
 20  AG          2.245E-10  0.0000000   -9.67764   0.935719     0.029     0.000
 60  H3ASO3      1.528E-26  0.0000000  -25.81536   1.000908     0.000     0.000
 61  H3ASO4      1.713E-15  0.0000000  -14.76580   1.000908     0.000     0.000
```

Sample Output No. 6

```
SPECIES:   TYPE  II - COMPLEXES

   ID          NAME          CALC MOL   ACTIVITY    LOG ACTVTY      GAMMA     NEW LOGK        DH
3302702   KH2F2 AQ         1.317E-20  0.0000000   -19.88015     1.000908      6.768       0.000
3305800   KHPO4 -2         1.449E-06  0.0000011    -5.95257     0.769943     12.601      -3.530
3305801   KH2PO4 -         2.053E-07  0.0000002    -6.71578     0.937182     19.763      -4.520
3300020   K OH-            3.197E-07  0.0000003    -6.52441     0.934977    -14.505      13.345
3307700   KH3SIO4 -        1.647E-06  0.0000015    -5.81218     0.935572    -10.273       8.935
3307701   KH2SIO4 -2       5.563E-11  0.0000000   -10.36739     0.771430    -22.754      29.714
7702700   KSIF6 -2         3.180E-37  0.0000000   -36.61116     0.769943     30.947     -16.260
3300900   KH2BO3 -1        2.074E-07  0.0000002    -6.71286     0.933753     -9.339       3.224
 902700   KBF(OH)3 -       7.727E-12  0.0000000   -11.14175     0.933753     -0.444       1.850
 902701   KBF2(OH)2 -      3.996E-17  0.0000000   -16.42816     0.933753      7.594       1.635
 902702   KBF3OH -         2.778E-24  0.0000000   -23.58599     0.933753     13.760      -1.580
 902703   KBF4 -           5.437E-31  0.0000000   -30.29440     0.933753     20.376      -1.795
3304900   KNH3 AQ          2.242E-23  0.0000000   -22.64893     1.000908     -9.747      12.480
4907320   KNH4SO4 -        9.166E-25  0.0000000   -24.06619     0.936731      1.138       0.000
4603300   KMGOH +          1.014E-08  0.0000000    -8.02146     0.938392    -12.373      15.935
4602700   KMGF +           5.193E-08  0.0000000    -7.31325     0.936157      1.661       4.674
4601400   KMGCO3 AQ        9.684E-07  0.0000010    -6.01355     1.000908      2.876       2.022
4601401   KMGHCO3 +        4.505E-06  0.0000042    -5.37525     0.935572     11.554      -2.430
4607320   KMGSO4 AQ        1.988E-06  0.0000020    -5.70127     1.000908      2.193       1.399
4605800   KMGPO4 -         2.697E-08  0.0000000    -7.59736     0.937182      6.493       3.100
4605801   KMGH2PO4 +       1.141E-09  0.0000000    -8.97074     0.937182     21.139      -1.120
4605802   KMGHPO4 AQ       1.436E-07  0.0000001    -6.84252     1.000908     15.229      -0.230
1503300   KCAOH +          5.118E-09  0.0000000    -8.31878     0.937848    -13.154      14.535
1501400   KCAHCO3 +        8.255E-06  0.0000077    -5.11113     0.937848     11.332       1.790
1501401   KCACO3 AQ        4.296E-06  0.0000043    -5.36652     1.000908      3.038       4.030
1507320   KCASO4 AQ        6.907E-06  0.0000069    -5.16035     1.000908      2.250       1.470
1505800   KCAHPO4 AQ       3.213E-07  0.0000003    -6.49274     1.000908     15.094      -0.230
1505801   KCAPO4 -         6.104E-08  0.0000001    -7.24259     0.937182      6.363       3.100
1505802   KCAH2PO4 +       2.730E-09  0.0000000    -8.59197     0.937182     21.033      -1.120
1502700   KCAF +           2.265E-08  0.0000000    -7.67326     0.936731      0.816       3.798
5001400   KNACO3 -         2.334E-08  0.0000000    -7.66006     0.937182      0.938       8.911
5001401   KNAHCO3 AQ       3.160E-07  0.0000003    -6.49989     1.000908     10.080       0.000
5007320   KNASO4 -         1.283E-07  0.0000001    -6.92004     0.937182      0.683       1.120
5005800   KNAHPO4 -        8.174E-10  0.0000000    -9.11575     0.937182     12.664       0.000
5002700   KNAF AQ          3.839E-10  0.0000000    -9.41537     1.000908     -0.790       0.000
4107320   KKSO4 -          1.028E-08  0.0000000    -8.01635     0.937182      0.751       2.250
4105800   KKHPO4 -         5.652E-11  0.0000000   -10.27600     0.937182     12.668       0.000
 303300   KALOH +2         6.546E-13  0.0000000   -12.29674     0.771430     -5.356      11.899
 303301   KAL(OH)2 +       1.287E-09  0.0000000    -8.91850     0.937182    -10.072       0.000
 303302   KAL(OH)4 -       2.878E-08  0.0000000    -7.56950     0.936157    -24.742      44.060
 302700   KALF +2          9.336E-14  0.0000000   -13.14253     0.771430      7.123       0.000
 302701   KALF2 +          3.219E-14  0.0000000   -13.52048     0.937182     11.974      20.000
 302702   KALF3 AQ         1.375E-14  0.0000000   -13.86116     1.000908     16.919       2.500
 302703   KALF4 -          4.507E-17  0.0000000   -16.37475     0.936157     19.749       0.000
 307320   KALSO4 +         7.245E-17  0.0000000   -16.16860     0.936157      2.962       2.150
 307321   KAL(SO4)2 -      2.942E-19  0.0000000   -18.56006     0.936157      4.835       2.840
 303303   KAL(OH)3 AQ      1.553E-07  0.0000002    -6.80852     1.000908    -16.000       0.000
2803300   KFEOH +          1.402E-14  0.0000000   -13.88156     0.936731    -10.002      13.199
2803301   KFEOH3 -1        9.537E-21  0.0000000   -20.04897     0.936731    -32.189      30.300
2807320   KFESO4 AQ        9.886E-15  0.0000000   -14.00457     1.000908      2.120       3.230
```

Sample Output No. 7

```
   SPECIES:   TYPE  III - FIXED SOLIDS
      ID  NAME        CALC MOL      LOG MOL    NEW LOGK      DH
       2  H2O          -2.524E-05     -4.598       0.000       0.000
       1  E             6.309E-05     -4.200       7.840       0.000
     330  H            -1.825E-03     -2.739       8.010       0.000
 2812800  FE+3/FE+2    -2.686E-07     -6.571      13.434     -10.000
 2302310  CU+1/CU+2    -3.148E-09     -8.502       2.654       1.650
 4714700  MN+3/MN+2    -4.005E-08     -7.397     -26.542      25.760
 4904920  NH4/NO3      -7.984E-06     -5.098     126.596    -187.055
 4914920  NO2/NO3       5.196E-07     -6.284      30.329     -43.760
  600610  ASO3/ASO4    -1.335E-08     -7.874      20.650     -30.015


   SPECIES:   TYPE  IV - PRECIPITATED SOLIDS

    ID         NAME        CALC MOL      LOG MOL    NEW LOGK      DH
 5015001  CALCITE       9.936E-02     -3.196       8.405       2.585


   SPECIES:   TYPE  V - DISSOLVED SOLIDS

    ID         NAME        CALC MOL      LOG MOL    NEW LOGK      DH
 2028100  FERRIHYDRITE  4.830E+01      1.684      -4.891       0.000
 6015001  GYPSUM        1.586E-03     -2.800       4.610      -0.261
 2077004  SIO2(A,PT)    2.223E-01     -0.653       2.867      -3.910


   SPECIES:   TYPE  VI - SPECIES NOT CONSIDERED

    ID         NAME        CALC MOL      LOG MOL    NEW LOGK      DH
 3300021  O2(AQ) SATO   7.244E+17     17.860     -45.540       0.000
 3300022  O2(AQ) CALC   1.098E-28    -27.959     -91.359     133.830
 3300023  O2(GAS)       6.141E-26    -25.212     -88.612     136.630
 4700021  KMNO4 -2      5.640E-37    -36.249    -124.470     150.020
 4700020  KMNO4 -       0.000E+00    -38.862    -134.923     176.620
 3301404  CH4(GAS)      0.000E+00   -104.547      43.532     -61.000
 3301403  CO2(GAS)      7.993E-04     -3.097      18.181      -0.530
```

Sample Output No. 8

```
PERCENTAGE DISTRIBUTION OF COMPONENTS

NA
        99.9     PERCENT BOUND IN SPECIES #    500    NA

K
       100.0     PERCENT BOUND IN SPECIES #    410    K

CA
        97.9     PERCENT BOUND IN SPECIES #    150    CA

MG
        97.5     PERCENT BOUND IN SPECIES #    460    MG
         1.5     PERCENT BOUND IN SPECIES #4601401    KMGHCO3 +

H4SIO4
        99.5     PERCENT BOUND IN SPECIES #    770    H4SIO4

PB
         1.3     PERCENT BOUND IN SPECIES #    600    PB
         1.7     PERCENT BOUND IN SPECIES #6001400    KPB(CO3)2-2
         2.1     PERCENT BOUND IN SPECIES #6003300    KPBOH +
        93.9     PERCENT BOUND IN SPECIES #6001401    KPBCO3 AQ

CL
       100.0     PERCENT BOUND IN SPECIES #    180    CL
SO4
        88.7     PERCENT BOUND IN SPECIES #    732    SO4
         2.5     PERCENT BOUND IN SPECIES #4607320    KMGSO4 AQ
         8.6     PERCENT BOUND IN SPECIES #1507320    KCASO4 AQ
```

Sample Output No. 9

```
IDX  NAME       AQUEOUS MASS  SORBED MASS
500  NA               5.221E-04    0.000E+00
410  K                3.581E-05    0.000E+00
150  CA               9.409E-04    0.000E+00
460  MG               3.086E-04    0.000E+00
770  H4SIO4           3.031E-04    0.000E+00
600  PB               1.448E-10    0.000E+00
180  CL               2.793E-04    0.000E+00
732  SO4              8.017E-05    0.000E+00
 90  H3BO3            4.626E-06    0.000E+00
130  BR               7.510E-08    0.000E+00
380  I                1.419E-08    0.000E+00
270  F                5.265E-06    0.000E+00
580  PO4              2.212E-06    0.000E+00
492  NO3              2.195E-05    0.000E+00
230  CU+1             2.232E-16    0.000E+00
 20  AG               3.709E-10    0.000E+00
280  FE+2             1.809E-12    0.000E+00
540  NI               3.066E-08    0.000E+00
470  MN+2             8.011E-08    0.000E+00
 60  H3ASO3           1.582E-26    0.000E+00
 30  AL               1.853E-07    0.000E+00
950  ZN               7.497E-09    0.000E+00
160  CD               8.899E-10    0.000E+00
  2  H2O              1.796E-06    0.000E+00
491  NO2              9.327E-07    0.000E+00
490  NH4              1.333E-21    0.000E+00
281  FE+3             2.812E-07    0.000E+00
231  CU+2             7.870E-09    0.000E+00
471  MN+3             2.073E-26    0.000E+00
  1  E                0.000E+00    0.000E+00
 61  H3ASO4           2.670E-08    0.000E+00
330  H                1.904E-03    0.000E+00
140  CO3              1.869E-03    0.000E+00
```

Sample Output No. 10

```
    CHARGE BALANCE: SPECIATED
      SUM OF CATIONS =  3.014E-03 SUM OF ANIONS   2.265E-03
        PERCENT DIFFERENCE =   1.419E+01   (ANIONS - CATIONS)/(ANIONS + CATIONS)
   NONCARBONATE ALKALINITY =   0.000E+00
IONIC STRENGTH = :  3.941E-03
```

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Sample Output No. 11

```
SATURATION INDICES FOR ALL MINERALS AND SOLIDS

  ID      NAME            LOG SI    LOG K    MIN LOGK  MAX LOGK   LOG IAP     DH
2003000  ALOH3(A)        -2.276   -11.467   -10.777    -1.087     9.191   27.045
6003000  ALOHSO4         -7.862     3.230     3.390     3.070   -11.092    0.000
6003001  AL4(OH)10SO4    -6.218   -22.700     0.000     0.000    16.482    0.000
6041000  ALUM K         -22.332     5.460     0.290     0.290   -27.842   -7.220
6041001  ALUNITE         -7.955     1.503     0.157     0.157    -9.458   -3.918
6015000 ANHYDRITE        -2.925     4.486    -0.151    -0.151    -7.410    3.769
5015000 ARAGONITE        -0.198     8.207    -0.105    -0.105    -8.405    2.615
5046000 ARTINITE         -7.257   -10.755    -1.155    -1.155     3.499   28.742
2003001 BOEHMITE         -0.517    -9.709    -9.196    -1.131     9.192   28.130
2046000 BRUCITE          -5.442   -17.831    -1.039    -1.039    12.389   25.840
5015001 CALCITE           0.000     8.405     8.456    -0.104    -8.405    2.585
2077000 CHALCEDONY        0.188     3.708     0.185     0.185    -3.520   -4.615
8646000 CHRYSOTILE       -4.172   -34.298    -2.110    -2.110    30.125   52.485
8246000 CLINOENSTITE     -3.274   -12.142   -11.776   -12.436     8.868   20.015
2077001 CRISTOBALITE      0.288     3.808     0.221     0.221    -3.520   -5.500
2003002 DIASPORE          1.329    -7.863    -0.990    -0.990     9.192   24.630
8215000 DIOPSIDE         -2.962   -21.183    -1.297    -1.297    18.221   32.280
5015002 DOLOMITE         -0.628    16.667    -0.333    -0.333   -17.295    8.290
6046000 EPSOMITE         -5.642     2.253     0.113     0.113    -7.895   -2.820
8646003 SEPIOLITE(C)     -2.793   -17.009    -1.096    -1.096    14.216   27.268
2028100 FERRIHYDRITE      1.684    -4.891    -1.557    -4.996     6.575    0.000
2028101 FE3(OH)8         -2.913   -20.222   -17.112   -24.105    17.309    0.000
4128100 FEOH)2.7CL.3      6.137     3.040     0.000     0.000     3.097    0.000
6028100 FE2(SO4)3       -53.657    -5.956    -1.726    -2.376   -47.701   59.120
7015002 FCO3APATITE      14.833   115.983     1.583     1.583  -101.150  -39.390
4215000 FLUORITE         -2.621    11.153     0.189     0.189   -13.775   -4.710
8046000 FORSTERITE       -8.991   -30.248    -1.950    -1.950    21.257   48.510
2003003 GIBBSITE (C)     -0.495    -9.686    -9.403   -10.356     9.191   22.800
2028102 GOETHITE          5.493    -1.082    -0.582    -0.582     6.575   14.480
8628000 GREENALITE      -15.374   -20.810     0.000     0.000     5.436    0.000
6015001 GYPSUM           -2.552     4.858     0.010     0.010    -7.410   -0.261
4150000 HALITE           -8.440    -1.545     0.037     0.037    -6.895   -0.918
2028105 HEMATITE         15.918     2.768    -1.240    -1.240    13.150   30.845
5015003 HUNTITE          -6.142    28.933    -1.035    -1.035   -35.075   25.760
5046001 HYDRMAGNESIT    -16.504     6.667    -2.099    -2.099   -23.171   52.210
6050000 JAROSITE NA      -6.398     9.746    -1.454    -1.454   -16.144   36.180
6041002 JAROSITE K       -3.765    13.543    -1.257    -1.257   -17.308   31.280
6028101 JAROSITE H      -10.959     9.883    -2.217    -2.217   -20.842   55.150
8450000 MAGADIITE        -5.644    14.300     0.000     0.000   -19.944    0.000
2028104 MAGHEMITE         6.764    -6.386     0.000     0.000    13.150    0.000
5046002 MAGNESITE        -1.109     7.781     8.031     7.531    -8.890    6.169
3028000 MAGNETITE        11.54     -5.765    -5.395    -8.623    17.309   50.460
6028000 MELANTERITE     -13.540     2.585     0.115     0.115   -16.125   -2.860
6050001 MIRABILITE       -9.009     1.877     0.763     0.763   -10.887 - 18.987
3050000 NATRON           -9.938     1.944     0.633     0.633   -11.881 - 15.745
5046003 NESQUEHONITE     -3.502     5.388     4.900     4.313    -8.890    5.789
8646001 PHLOGOPITE      -30.440   -69.771    -3.471    -3.471    39.331   86.360
2077002 QUARTZ            0.736     4.256     0.250     0.250    -3.520   -6.220
8646004 SEPIOLITE(A)     -4.564   -18.780     0.000     0.000    14.216    0.000
5028000 SIDERITE         -6.784    10.336    11.890    -0.214   -17.120    5.328
2077003 SIO2(A,GL)       -0.324     3.196     0.178     0.178    -3.520   -4.440
2077004 SIO2(A,PT)       -0.653     2.867     0.157     0.157    -3.520   -3.910
7028100 STRENGITE        -1.567    26.318    29.041    26.153   -27.885    2.030
8646002 TALC             -1.377   -24.462   -20.395   -24.495    23.085   35.005
6050002 THENARDITE      -10.730     0.156    -0.023    -0.023   -10.886    0.572
5050001 THERMONATR      -12.119    -0.238    -0.113    -0.113   -11.881    2.802
8215001 TREMOLITE        -0.902   -60.429    -3.883    -3.883    59.528   96.615
7028001 VIVIANITE       -20.444    36.000     0.000     0.000   -56.444    0.000
2047000 PYROLUSITE       -3.075   -17.034    -1.173   -17.211    13.959   29.180
2047001 BIRNESSITE       -4.132   -18.091     0.000     0.000    13.959    0.000
2047002 NSUTITE          -3.545   -17.504     0.000     0.000    13.959    0.000
```

The number of iterations that MINTEQ took to converge and the name of the component whose convergence criteria are given are listed under the headings "ITER" and "NAME", respectively. The "TOTAL MOLALITY" in sample output No. 3 refers to the total analytical molality input for the designated Type 1 species (components). For example, sodium has a total input molality of 5.221E-04 (12 mg/L). The molality of the calcium, "CA", differs from the mass of calcium that was entered because this mass was modified by the calcium carbonate designated as a Type 4 species. The heading "DIFF FXN" stands for difference function. The difference function is the difference between the analytical mass of the component that was input and the mass of the same component calculated at this point in the convergence procedure. Hopefully, this number for any particular component will grow smaller as you go through successive iterations. The column "LOG ACTVTY" gives what MINTEQ calculates for the log of the activity of the indicated component at the specified stage in the iterative process. The log activity will change in progressive iterations because of changes in ion speciation and activity coefficient calculations.

Sample output No. 4 contains information from the initial equilibration of the chemical problem posed in the input file. In a simple ion speciation/solubility run, this would also be the final equilibration of the chemical problem. In the case where solids are considered, this information is for the equilibration of the initial input solution with any designated Type 4 species (e.g., calcium carbonate). The total input analytical molality of a species (Type 1 species) is given under "ANAL MOL".

The "CALC MOL" represents the calculated molality of the particular form of the species in which the component is expressed. For example, the analytical molality for calcium is the total calcium in solution. The total calcium in solution includes the Ca^{2+} and all the other complexes of calcium that exist in solution. The calculated molality refers to the concentration of the Ca^{2+} species (our calcium component) only. Thus the "CALC MOL" will usually be smaller than the "ANAL MOL". In our example, the calculated molality ("CALC MOL") for calcium is larger than the analytical molality ("ANAL MOL") because of the calcium that came into solution from the dissolution of the calcium carbonate.

"ACTIVITY" gives us the activity of the component calculated from "CALC MOL" and "GAMMA" where "GAMMA" is the activity coefficient of the component and "LOG ACTVTY" is the log of the component activity (ACTIVITY). This "LOG ACTVTY" is different from the "LOG ACTVTY" given in sample output No. 3. The "LOG ACTVTY" in sample output No. 3 is the log of the activity of the component at a certain stage in the iterative process, while the "LOG ACTVTY" in sample output 4 is the final log activity computed for the indicated component. The new log K (NEW LOGK) for components is the negative of the log of the activity coefficient (GAMMA). For most species (e.g., complexes), the new log K would be the log K for the reaction in the data base modified by the activity

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coefficients of the species that constitute the formation reaction for the complex. However, for components, the log K is 0; therefore, the log of the activity coefficient of the component is subtracted from 0 to give the new log K. The difference function (DIFF FXN) was explained previously.

Sample output No. 5 contains much of the same information given in sample output No. 4, except this output file has a column for the enthalpy of reaction (DH). "DH" is a meaningless term for the components because reactions are written in terms of components in MINTEQ.

Information on the complexes formed in solution is provided in the column headings shown in sample output No. 5. The identification number of a complex is listed under the heading "ID" followed on the same line by the name of the complex (under the heading "NAME"). All the other headings for the TYPE 2 species were already explained previously, except for "NEW LOGK" and "DH". The new log K is the log K in the data base modified by the activity coefficient corrections if the temperature of your solution is 25C or there is no enthalpy of reaction (DH) available. If the temperature is other than 25C and an enthalpy of reaction is available (or analytical expressions for the log K as a function of temperature), the new log K will be different from the log K in the data base modified by the activity coefficient corrections. The new log K in this case will additionally be affected by the temperature corrections.

The output for Types 3, 4, 5, and 6 species are shown in sample output No. 7 (we will continue using arabic numerals to represent the roman numerals given on the actual output). We will only explain those output headings that were not covered in previous discussions or that need further elaboration. Some headings are repeated in each of the output sections but require additional explanation because the headings may have different meanings for different species types. The calculated molality (CALC MOL) for Type 3 redox couples represents the amount the redox ratio had to be adjusted to conform to the imposed pe. The calculated molalities for the H2O and H give the amounts of each that were taken from a source or given to a sink to balance the equilibrium equations. These data usually provide nothing in the way of interpreting the data we are modeling. The calculated molality of the Type 4 species (calcite in this case) is the amount of the finite solid (calcite) that remains in the system after equilibration with the input solution. For this example, calcite has dissolved slightly going from an input of 1.000E-01 moles to 9.936E-02 moles. For Type 5 species, the calculated molality is the activity product divided by the new solubility product (NEW LOGK), while "LOG MOL" is just the log of the calculated molality. The calculated molality "CALC MOL" for Type 6 species is the molality the species would have had if it had been included in the equilibrium calculations. Remember that Type 6 species are species that were excluded from the equilibrium calculations.

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MINTEQ also provides the percentage distribution of species as part of the output file (sample output No. 8). In the far left column, the component whose species distribution is considered is given. Below and to the right of each component are listed the species that compose approximately 1% or more of the total mass of the component. The identification number is also given in a separate column to the left of each species name.

In sample output No. 9, under the corresponding column headings from left to right, are the identification number (IDX) of the component, the name of the component, the aqueous mass of the the component, and the sorbed mass of the component. Because no adsorption algorithm was used there is no mass in the "SORBED MASS" column. The "AQUEOUS MASS" is equal to the total input mass, and any contribution to the concentration resulting from the dissolution of any Type 4 solids. For this reason, the mass of calcium is larger than the input mass because of the calcium carbonate that dissolved to reach equilibrium with the solution.

Sample output No. 10 has information on the equivalents of anions and cations and the charge balance after the solution is speciated. The ionic strength and noncarbonate alkalinity are also given. The percent difference in the charge balance between the speciated and unspeciated runs may differ significantly, if for example, you have entered your carbonate data as alkalinity. Also, if the partial pressure of CO_2 is fixed, this may cause the speciated portion of the output to be considerably different from the unspeciated portion because the CO_2 (and thus CO_3) is being pumped into or out of the system. Additionally, when the pH is fixed, you can protonate species and cause the charge balance to change.

The saturation indices for all minerals and solids whose components are entered into the input file are included in the output (sample output No. 11). The identification numbers and names of the minerals and solids are included in the first two columns. The "LOG SI" or log of the saturation index begins in the third column. The log of the saturation index is normally computed by placing the log of the activity product (LOG IAP) over the log of the solubility product (LOG K) (based on a dissolution reaction) so that log SI = Log IAP - Log K. However, in MINTEQ, the mineral and solid phase reactions are written as formation reactions instead of dissolution reactions. The log K, therefore, is the negative of the log K written as a dissolution reaction, and the "LOG SI" in the output is calculated by adding together the "LOG IAP" and the "LOG K". The only other columns that have not already been discussed are "MIN LOGK" and "MAX LOGK". These headings refer, respectively, to the minimum and maximum values for the log K that are entered in the data base. They are printed, if available, for the information of the user.

If solids are considered (allowed to precipitate or dissolve), as in this example, MINTEQ will reequilibrate the solution after each solid precipitates or dissolves. MINTEQ will then similarly print out information on the iterations for sample output No. 3 after each equilibration. As each solid precipitates or dissolves, MINTEQ will name the solid that is dissolved or precipitated. After all solids are equilibrated with the solution or are completely dissolved, MINTEQ again prints out information on all the species types and the aqueous masses of all components, etc. This output is similar to the output already discussed. In summary, if solids are dissolving or precipitating, MINTEQ will print information on two equilibrations of the solution, one before all solids are considered and another after the solids are considered.

REFERENCES

Ball, J. W., E. A. Jenne and M. W. Cantrell. 1981. *WATEQ3: A Geochemical Model with Uranium Added*. U.S. Geological Survey, Open-File Report 81-1183.

Ball, J. W., D. K. Nordstrom and E. A. Jenne. 1980. *Additional and Revised Thermochemical Data and Computer Code for WATEQ2-A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters*. U.S. Geological Survey, Water Resources Investigations WRI-78-116.

CODATA Task Group. 1977. "CODATA Recommended Key Values for Thermodynamics, 1977. Report of the CODATA Task Group on Key Values for Thermodynamics, 1977." *J. Chem. Thermodynamics* 10:903-906.

Cowan, C. E., E. A. Jenne and R. R. Kinnison. 1984. "A Methodology for Determining the Toxic Chemical Species of Copper in Toxicity Experiments and Natural Waters." Paper presented at the 18th Annual Conference on Trace Substances in Environmental Health, June 4-7, 1984, Columbia, Missouri.

Dana, E. S., and W. E. Ford. 1957. *A Textbook of Mineralogy*. John Wiley and Sons, Inc., New York, New York.

Davies, C. W. 1962. *Ion Association*. Butterworths Publisher, Washington, D.C.

Davis, J. A., R. O. James, and J. O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: I. Computation of Electrical Double Layer Properties in Simple Electrolytes." *J. Colloid Interface Sci*. 63:(3):480-499.

Davis, J. A., and J. O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions." *J. Colloid Interface Sci*. 67(1):90-107.

Davis, J. A., and J. O. Leckie. 1980." Surface Ionization and Complexation at the Oxide/Water Interface: 3. Adsorption of Anions." *J. Colloid Interface Sci.* 74(1):32-43.

Felmy, A. R., S. M. Brown, Y. Onishi, S. B. Yabusaki and R. S. Argo. 1984a. *MEXAMS--The Metals Exposure Analysis Modeling System*. (NTIS PB84-157155) EPA-600/3-84-031, National Technical Information Service, Springfield, Virginia.

Felmy, A. R., D. C. Girvin and E. A. Jenne. 1984b. MINTEQ: *A Computer Program for Calculating Aqueous Geochemical Equilibria*. (NTIS PB84-157148) EPA-600/3-84-032, National Technical Information Service, Springfield, Virginia.

Freeze, R. A., and J. A. Cherry. 1979. Groundwater. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Harvie, C. E., and J. H. Weare. 1980. "The Prediction of Mineral Solubilities in Natural Waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C." Geochim. et Cosmochim. Acta 44:981-987.

Jenne, E. A. 1981. Waste/Rock Interactions Technology Program Geochemical Modeling: A Review. PNL-3574, Pacific Northwest Laboratory, Richland, Washington.

Kincaid, C. T., J. R. Morrey and J. E. Rogers. 1984a. Geohydrochemical Models of Solute Migration, Volume 1. EA-3417, Electric Power Research Institute, Palo Alto, California.

Kincaid, C. T., J. R. Morrey, S. B. Yabusake, A. R. Felmy and J. E. Rogers. 1984b. Geohydrochemical Models for Solute Migration Volume 2: Preliminary Evaluation of Selected Computer Codes. EA-3417, Electric Power Research Institute, Palo Alto, California.

Lemire, R. L., and P. R. Tremaine. 1983. "Uranium and Plutonium Equilibria in Aeuqous Solutions to 200 C." J. Chem. Eng. Data 25:361-370.

Lindberg, R. D., and D. D. Runnells. 1984. "Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling." Science 31:925-927.

McDuff, R. E., and F. M. M. Morel. 1973. Description and Use of the Chemical Equilibrium Program REDEQL2. EQ-73-02, California Inst. of Tech., Pasadena, California.

Morel, F., and J. Morgan. 1972. "A Numerical Method for Computing Equilibria in Aqueous Systems." Environ. Sci. Technol. 6:56-67.

Morel, F. M. M. 1983. "Principles of Aquatic Chemistry." John Wiley and Sons, New York, New York.

Nordstrom, D. K., E. A. Jenne and J. W. Ball. 1979. "Redox Equilibria of Iron in Acid Mine Waters." In Chemical Modeling in Aqueous Systems, ed. E. A. Jenne, ACS Symposium Series No. 93:51-79, American Chemical Society, Washington, D.C.

Parkhurst, D. L., L. N. Plummer and D. C. Thorstenson. 1982. "BALANCE-A Computer Program for Calculating Mass Transfer for Geochemical Reactions in Groundwater". U.S. Geological Survey, Water-Resources Investigations 82-14.

Parkhurst, D. L., D. C. Thorstenson and L. N. Plummer. 1980. PHREEQE - A Computer Program for Geochemical Calculations. U.S. Geological Survey, Water-Resources Investigations 80-96.

Plummer, L. N. 1984. "Geochemical Modeling: A Comparison of Forward and Inverse Methods." In First Canadian/American Conference on Hydrogeology: Predicted Application of Ground Water Geochemistry, ed. B. Hichox and E. I. Wallick, pp. 149-177. National Waterwell Association, Worthington, Ohio.

Rard, J. A. 1983. Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species. UCRL-53440, Lawrence Livermore National Laboratory, University of California, Livermore, California.

Robie, R. A., B. S. Hemingway and F. R. Fisher. 1978. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures, U.S. Geol. Survey Bull. 1452, reprinted with corrections 1979, U.S. Government Printing Office, Washington, D.C.

Schmidt, R. L. 1984. Thermodynamic Properties and Environmental Chemistry of Chromium. PNL-4881, Pacific Northwest Laboratory, Richland, Washington.

Sposito, G., and S. V. Mattigod. 1980. GEOCHEM: A Computer Program for the Calculations of Chemical Equilibria in Soil Solutions and Other Natural Water Systems. University of California, Riverside, California.

Truesdell, A. H., and B. F. Jones. 1974. "WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters." U.S. Geol. Survey J. Res. 2:233-274.

Van Zeggeren, F., and S. H. Storey. 1970. The Computation of Chemical Equilibria. Cambridge University Press, England.

Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall. 1982. The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units. Vol. II, Supplement, American Chemical Society, New York.

Westall, J. C., J. L. Zachary and F. M. Morel. 1976. "MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems." Tech. Note 18, Dept. of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Wolery, T. J. 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQ3/6 Software Package. UCRL-52658, Lawrence Livermore Laboratory, University of California, Livermore, California.

Wolery, T. J. 1983. EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations. Lawrence Livermore Laboratory, Livermore, California.

APPENDIX A

COMPONENTS IN MINTEQ

APPENDIX A

COMPONENTS IN MINTEQ

TABLE A.1. Components in MINTEQ

Component	ID Number	Component	ID Number	Component	ID Number
E	001	Fe^{3+}	281	HSe^-	760
H_2O	002	H^+	330	$HSeO_3^-$	761
Ag^+	020	Hg_2^{2+}	360	SeO_4^{2-}	762
Al^{3+}	030	$Hg(OH)_2$	361	H_4SiO_4	770
H_3AsO_3	060	I^-	380	Sr^{2+}	800
H_3AsO_4	061	K^+	410	Th^{4+}	850
H_3BO_3	090	Li^+	440	$T\ell^+$	870
Ba^{2+}	100	Mg^{2+}	460	$T\ell(OH)_3$	871
Br^-	130	Mn^{2+}	470	U^{3+}	890
CO_3^{2-}	140	Mn^{3+}	471	U^{4+}	891
Fulvate	141	MoO_4^{2-}	480	UO_2^+	892
Humate	142	NH_4^+	490	UO_2^{2+}	893
Ca^{2+}	150	NO_2^-	491	V^{2+}	900
Cd^{2+}	160	NO_3^-	492	V^{3+}	901
Cl^-	180	Na^+	500	VO^{2+}	902
Cr^{2+}	210	Ni^{2+}	540	VO_2^+	903
$Cr(OH)_2^+$	211	PO_4^{3-}	580	Zn^{2+}	950
CrO_4^{2-}	212	Pb^{2+}	600	SOH1	990
Cs^+	220	Ra^{2+}	670	SOH2	991
Cu^+	230	Rb^+	680	XPSIO	992
Cu^{2+}	231	HS^-	730	XPSIB	993
F^-	270	S	731	XPSID	994
Fe^{2+}	280	SO_4^{2-}	732	SOHB	995

APPENDIX B

LISTING OF THERMODYNAMIC DATA AND ID NUMBERS

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LISTING OF THERMODYNAMIC DATA AND ID NUMBERS

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8703300 TlOH AQ       13.9350  -13.1717                 0.00 0.00 0.00 221.3773
 0.00 3     1.000 870     1.000   2    -1.000 330
8702700 TlF AQ         0.0000   -0.4251                 0.00 0.00 0.00 223.3684
 0.00 2     1.000 870     1.000 270
8701800 TlCl AQ       -1.1470    0.6824                 0.00 0.00 0.00 239.8230
 0.00 2     1.000 870     1.000 180
8701801 TlCl2-1        0.0000    0.2434                 -1.000.00 0.00 275.2760
 0.00 2     1.000 870     2.000 180
8701300 TlBr AQ       -2.4610    0.9477                 0.00 0.00 0.00 284.2740
 0.00 2     1.000 870     1.000 130
8701301 TlBr2-1        2.9980    0.9719                 -1.000.00 0.00 364.1780
 0.00 2     1.000 870     2.000 130
8701302 TlBrCl-1       0.0000    0.8165                 -1.000.00 0.00 319.7270
 0.00 3     1.000 870     1.000 130     1.000 180
8703800 TlI AQ         0.0000    1.4279                 0.00 0.00 0.00 331.2745
 0.00 2     1.000 870     1.000 380
8703801 TlI2-1         0.0000    1.8588                 -1.000.00 0.00 458.1790
 0.00 2     1.000 870     2.000 380
8703802 TlIBr-1        0.0000    2.1850                 -1.000.00 0.00 411.1785
 0.00 3     1.000 870     1.000 380     1.000 130
8707320 TlSO4-1       -0.2200    1.3853                 -1.000.00 0.00 300.4276
 0.00 2     1.000 870     1.000 732
8704920 TlNO3 AQ      -0.6500    0.3665                 0.00 0.00 0.00 266.3749
 0.00 2     1.000 870     1.000 492
8704910 TlNO2 AQ       0.0000    0.9969                 0.00 0.00 0.00 250.3755
 0.00 2     1.000 870     1.000 491
8707300 TlHS AQ        0.0000    1.8178                 0.00 0.00 0.00 237.4379
 0.00 2     1.000 870     1.000 730
8707301 Tl2HS+1        0.0000    7.6979                 1.00 0.00 0.00 441.8079
 0.00 2     2.000 870     1.000 730
8707302 Tl2OH(HS)3-    0.0000    1.0044                 -2.000.00 0.00 524.9510
 0.00 4     2.000 870     3.000 730     1.000   2    -1.000 330
8707303 Tl2(OH)2(HS    0.0000  -11.0681                 -2.000.00 0.00 508.8904
 0.00 4     2.000 870     2.000 730     2.000   2    -2.000 330
8713300 Tl+3           0.0000    4.7424                 3.00 0.00 0.00 204.3700
 0.00 3     1.000 871     3.000 330    -3.000   2
8713301 TlOH+2         0.0000    3.5770                 2.00 0.00 0.00 221.3773
 0.00 3     1.000 871     2.000 330    -2.000   2
8713302 Tl(OH)2+1      0.0000    2.1183                 1.00 0.00 0.00 238.3846
 0.00 3     1.000 871     1.000 330    -1.000   2
8711800 TlCl+2         0.0000   12.2342                 2.00 0.00 0.00 239.8230
 0.00 4     1.000 871     1.000 180     3.000 330    -3.000   2
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8711801 TlCl2+1        0.0000   18.0402                        1.00 0.00 0.00 275.2760
 0.00 4     1.000 871     2.000 180      3.000 330      -3.000   2
8711802 TlCl3 AQ       0.0000   21.4273                        0.00 0.00 0.00 310.7290
 0.00 4     1.000 871     3.000 180      3.000 330      -3.000   2
8711803 TlCl4-1        0.0000   24.2281                       -1.000.00 0.00 346.1820
 0.00 4     1.000 871     4.000 180      3.000 330      -3.000   2
8711300 TlBr+2         0.0000   14.2221                        2.00 0.00 0.00 284.2740
 0.00 4     1.000 871     1.000 130      3.000 330      -3.000   2
8711301 TLBr2+1        0.0000   21.5761                        1.00 0.00 0.00 364.1780
 0.00 4     1.000 871     2.000 130      3.000 330      -3.000   2
8711302 TlBr3 AQ       0.0000   27.0244                        0.00 0.00 0.00 444.0820
 0.00 4     1.000 871     3.000 130      3.000 330      -3.000   2
8711303 TlBr4-1        0.0000   31.1533                       -1.000.00 0.00 523.9860
 0.00 4     1.000 871     4.000 130      3.000 330      -3.000   2
8713800 TlI4-1         0.0000   34.7596                       -1.000.00 0.00 711.9880
 0.00 4     1.000 871     4.000 380      3.000 330      -3.000   2
8714920 TlNO3+2        0.0000    7.0073                        2.00 0.00 0.00 266.3749
 0.00 4     1.000 871     1.000 492      3.000 330      -3.000   2
8713303 Tl(OH)4-1      0.0000  -10.2545                       -1.000.00 0.00 272.3992
 0.00 3     1.000 871     1.000   2     -1.000 330
8711804 TlOHCl+1       0.0000   10.6290                        1.00 0.00 0.00 256.8303
 0.00 4     1.000 871     1.000 180      2.000 330      -2.000   2
3307601 Se-2          11.5000  -14.9529                       -2.000.00 0.00 78.9600
 0.00 2     1.000 760    -1.000 330
3307600 H2Se           0.8000    3.8115                        0.00 0.00 0.00 80.9758
 0.00 2     1.000 760     1.000 330
4707600 MnSe           0.0000   -6.7435                        0.00 0.00 0.00 133.8980
 0.00 3     1.000 760     1.000 470     -1.000 330
 207600 Ag2Se          0.0000   34.0677                        0.00 0.00 0.00 294.6960
 0.00 3     1.000 760     2.000  20     -1.000 330
 207601 AgOH(Se)2-4    0.0000  -18.6237                       -4.000.00 0.00 282.7953
 0.00 4     2.000 760     1.000  20      1.000   2      -3.000 330
3307611 SeO3-2         1.2800   -7.3005                       -2.000.00 0.00 126.9582
 0.00 2     1.000 761    -1.000 330
3307610 H2SeO3         1.6900    2.5728                        0.00 0.00 0.00 128.9740
 0.00 2     1.000 761     1.000 330
2817610 FeHSeO3+2      0.0000    1.8618                        2.00 0.00 0.00 183.8131
 0.00 2     1.000 761     1.000 281
 207610 AgSeO3-1       0.0000   -5.5985                       -1.000.00 0.00 234.8262
 0.00 3     1.000 761     1.000  20     -1.000 330
 207611 Ag(SeO3)2-3    0.0000  -10.9933                       -3.000.00 0.00 361.7844
 0.00 3     2.000 761     1.000  20     -2.000 330
1607610 Cd(SeO3)2-2    0.0000  -11.1890                       -2.000.00 0.00 366.3264
 0.00 3     2.000 761     1.000 160     -2.000 330
3307620 HSeO4-1        4.2000    1.9058                       -1.000.00 0.00 143.9655
 0.00 2     1.000 762     1.000 330
4707620 MnSeO4         3.4600    2.4188                        0.00 0.00 0.00 197.8955
 0.00 2     1.000 762     1.000 470
2007620 CoSeO4         2.9100    2.7120                        0.00 0.00 0.00 201.8908
 0.00 2     1.000 762     1.000 200
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5407620 NiSe04          3.5000    2.6387                       0.00 0.00 0.00 201.6576
 0.00 2      1.000 762      1.000 540
1607620 CdSe04          0.0000    2.2415                       0.00 0.00 0.00 255.3676
 0.00 2      1.000 762      1.000 160
9507620 ZnSe04          0.0000    2.2019                       0.00 0.00 0.00 208.3376
 0.00 2      1.000 762      1.000 950
9507621 Zn(Se04)2-2     0.0000    -0.0704                     -2.000.00 0.00 351.2952
 0.00 2      2.000 762      1.000 950
3600000 Hg (aq)       -16.6050    6.9316                       0.00 0.00 0.00 200.5900
 0.00 2      0.500 360      1.000   1
3613300 Hg+2          -11.0600    6.0970                       2.00 0.00 0.00 200.5900
 0.00 3      1.000 361      2.000 330    -2.000    2
3611301 HgBr+           0.0000    15.8347                      1.00 0.00 0.00 280.4940
 0.00 4      1.000 361      1.000 130     2.000 330    -2.000    2
3611302 HgBr2 (aq)    -30.8320    23.6065                      0.00 0.00 0.00 360.3980
 0.00 4      1.000 361      2.000 130     2.000 330    -2.000    2
3611303 HgBr3-1         0.0000    25.7857                     -1.000.00 0.00 440.3020
 0.00 4      1.000 361      2.000 330     3.000 130    -2.000    2
3611304 HgBr4-2         0.0000    27.0633                     -2.000.00 0.00 520.2060
 0.00 4      1.000 361      2.000 330     4.000 130    -2.000    2
3611305 HgBrCl (aq)     0.0000    22.0145                      0.00 0.00 0.00 315.9470
 0.00 5      1.000 361      1.000 130     1.000 180     2.000 330     -2.000    2
3611306 HgBrI (aq)      0.0000    27.1212                      0.00 0.00 0.00 407.3985
 0.00 5      1.000 361      1.000 130     1.000 380     2.000 330     -2.000    2
3611307 HgBrI3-2        0.0000    34.2135                     -2.000.00 0.00 661.2075
 0.00 5      1.000 361      1.000 130     3.000 380     2.000 330     -2.000    2
3611308 HgBr2I2-2       0.0000    32.3994                     -2.000.00 0.00 614.2070
 0.00 5      1.000 361      2.000 130     2.000 380     2.000 330     -2.000    2
3611309 HgBr3I-2        0.0000    30.1528                     -2.000.00 0.00 567.2065
 0.00 5      1.000 361      3.000 130     1.000 380     2.000 330     -2.000    2
3613301 HgBrOH (aq)     0.0000    11.5980                      0.00 0.00 0.00 297.5013
 0.00 4      1.000 361      1.000 130     1.000 330    -1.000    2
3611800 HgCl+1          0.0000    12.8500                      1.00 0.00 0.00 236.0430
 0.00 4      1.000 361      1.000 180     2.000 330    -2.000    2
3611801 HgCl2 (aq)      0.0000    19.2203                      0.00 0.00 0.00 271.4960
 0.00 4      1.000 361      2.000 180     2.000 330    -2.000    2
3811802 HgCl3-1         0.0000    20.1226                     -1.000.00 0.00 306.9490
 0.00 4      1.000 361      3.000 180     2.000 330    -2.000    2
3611803 HgCl4-2         0.0000    20.5338                     -2.000.00 0.00 342.4020
 0.00 4      1.000 361      4.000 180     2.000 330    -2.000    2
3611804 HgClI (aq)      0.0000    25.3532                      0.00 0.00 0.00 362.9475
 0.00 5      1.000 361      1.000 180     1.000 380     2.000 330     -2.000    2
3611805 HgClOH (aq)   -12.4820    9.3170                       0.00 0.00 0.00 253.0503
 0.00 4      1.000 361      1.000 180     1.000 330    -1.000    2
3612701 HgF+1           0.0000    8.0848                       1.00 0.00 0.00 219.5884
 0.00 4      1.000 361      1.000 270     2.000 330    -2.000    2
3613801 HGI+1           0.0000    18.8949                      1.00 0.00 0.00 327.4945
 0.00 4      1.000 361      1.000 380     2.000 330    -2.000    2
3613802 HgI2 (aq)     -44.5220    30.1081                      0.00 0.00 0.00 454.3990
 0.00 4      1.000 361      2.000 380     2.000 330    -2.000    2
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3613803 HgI3-1        -47.9430   33.7935                           -1.000.00 0.00 581.3035
 0.00 4      1.000 361      3.000 380        2.000 330      -2.000    2
3613804 HgI4-2          0.0000   35.7858                           -2.000.00 0.00 708.2080
 0.00 4      1.000 361      4.000 380        2.000 330      -2.000    2
3614900 HgNH3+2         0.0000    5.6139                            2.00 0.00 0.00 217.6204
 0.00 4      1.000 361      1.000 490        1.000 330      -2.000    2
3614901 Hg(NH3)2+2      0.0000    5.0341                            2.00 0.00 0.00 234.6508
 0.00 3      1.000 361      2.000 490       -2.000    2
3614902 Hg(NH3)3+2      0.0000   -3.2493                            2.00 0.00 0.00 251.6812
 0.00 4      1.000 361      3.000 490       -1.000 330      -2.000    2
3614903 Hg(NH3)4+2      0.0000  -11.7307                            2.00 0.00 0.00 268.7116
 0.00 4      1.000 361      4.000 490       -2.000 330      -2.000    2
3614920 HgNO3+1         0.0000    6.4503                            1.00 0.00 0.00 262.5949
 0.00 4      1.000 361      1.000 492        2.000 330      -2.000    2
3614921 Hg(NO3)2 (a     0.0000    4.7791                            0.00 0.00 0.00 324.5998
 0.00 4      1.000 361      2.000 492        2.000 330      -2.000    2
3613302 HgOH+1          0.0000    2.6974                            1.00 0.00 0.00 217.5973
 0.00 3      1.000 361      1.000 330       -1.000    2
3613303 Hg(OH)3-1       0.0000  -15.0042                           -1.000.00 0.00 251.6119
 0.00 3      1.000 361      1.000   2       -1.000 330
3617300 HgS2-2          0.0000   31.2398                           -2.000.00 0.00 264.7100
 0.00 3      1.000 361      2.000 730       -2.000    2
3617301 Hg(HS)2 (aq     0.0000   43.8178                            0.00 0.00 0.00 266.7258
 0.00 4      1.000 361      2.000 730        2.000 330      -2.000    2
3617320 HgSO4 (aq)      0.0000    7.4911                            0.00 0.00 0.00 296.6476
 0.00 4      1.000 361      1.000 732        2.000 330      -2.000    2
3611401 HgCH3NH2+2      0.0000   29.3846                            2.00 0.00 0.00 231.6472
 0.00 6      1.000 361      1.000 140      1.000 490      6.000 1 9.000 330 -5.000 2
3611402 Hg(CH3NH2)2   -87.3400   53.2132                            2.00 0.00 0.00 262.7044
 0.00 6      1.000 361      2.000 140    2.000 490     12.000 1  16.000 330  -8.000 2
2113300 Cr+3          -20.1400   10.2031                            3.00 0.00 0.00 51.9960
 0.00 3      1.000 211      2.000 330       -2.000    2
2113301 Cr(OH)+2        0.0000    6.3700                            2.00 0.00 0.00 69.0033
 0.00 3      1.000 211      1.000 330       -1.000    2
2110020 Cr(OH)3 AQ      0.0000   -7.7916                            0.00 0.00 0.00 103.0179
 0.00 3      1.000 211      1.000   2       -1.000 330
2110021 Cr(OH)4-        0.0000  -17.4000                           -1.000.00 0.00 120.0252
 0.00 3      1.000 211      2.000   2       -2.000 330
2113304 CrO2-           0.0000  -17.7456                           -1.000.00 0.00 83.9948
 0.00 2      1.000 211     -2.000 330
2111300 CrBR+2        -11.2110    7.5519                            2.00 0.00 0.00 131.9000
 0.00 4      1.000 211      1.000 130        2.000 330      -2.000    2
2111800 CrCL+2        -13.8470    9.3683                            2.00 0.00 0.00 87.4490
 0.00 4      1.000 211      1.000 180        2.000 330      -2.000    2
2111801 CrCL2 +        -9.3740    8.6580                            1.00 0.00 0.00 122.9020
 0.00 4      1.000 211      2.000 180        2.000 330      -2.000    2
2111802 CrOHCL2 AQ      0.0000    2.9627                            0.00 0.00 0.00 139.9093
 0.00 4      1.000 211      2.000 180        1.000 330      -1.000    2
2112700 CrF+2         -16.7890   14.5424                            2.00 0.00 0.00 70.9944
 0.00 4      1.000 211      1.000 270        2.000 330      -2.000    2
2113800 CrI+2          0.0000     4.8289                2.00 0.00 0.00 178.9005
 0.00 4     1.000 211     1.000 380     2.000 330   -2.000    2
2114900 Cr(NH3)6+3     0.0000   -32.5709                3.00 0.00 0.00 154.1784
 0.00 4     1.000 211     6.000 490    -4.000 330   -2.000    2
2114901 CrNH3)5OH+2    0.0000   -30.2759                2.00 0.00 0.00 154.1553
 0.00 4     1.000 211     5.000 490    -4.000 330   -1.000    2
2114902 CCrNH3)4OH2    0.0000   -29.8574                1.00 0.00 0.00 154.1322
 0.00 3     1.000 211     4.000 490    -4.000 330
2114903 TCrNH3)4OH2    0.0000   -30.5537                1.00 0.00 0.00 154.1322
 0.00 3     1.000 211     4.000 490    -4.000 330
2114904 CrNH3)6CL+2    0.0000   -31.7932                2.00 0.00 0.00 189.6314
 0.00 5     1.000 211     6.000 490     1.000 180   -2.000    2    -4.000 330
2114905 CrNH3)6BR+2    0.0000   -31.8870                2.00 0.00 0.00 234.0824
 0.00 5     1.000 211     6.000 490     1.000 130   -4.000 330    -2.000    2
2114906 CrNH3)6I +2    0.0000   -32.0080                2.00 0.00 0.00 281.0829
 0.00 5     1.000 211     6.000 490     1.000 380   -4.000 330    -2.000    2
2114920 CrNO3 +2     -15.6400     8.2094                2.00 0.00 0.00 114.0009
 0.00 4     1.000 211     1.000 492     2.000 330   -2.000    2
2115800 CrH2PO4 +2     0.0000    31.9068                2.00 0.00 0.00 148.9832
 0.00 4     1.000 211     4.000 330     1.000 580   -2.000    2
2117320 CrSO4 +      -12.6200    10.9654                1.00 0.00 0.00 148.0536
 0.00 4     1.000 211     1.000 732     2.000 330   -2.000    2
2117321 CrOHSO4 AQ     0.0000     8.2754                0.00 0.00 0.00 165.0609
 0.00 4     1.000 211     1.000 732     1.000 330   -1.000    2
2117322 Cr2OH2SO4)S    0.0000    14.5278                0.00 0.00 0.00 330.1218
 0.00 4     2.000 211     2.000 732     2.000 330   -2.000    2
2117323 Cr2OH2SO4+2    0.0000    16.1550                2.00 0.00 0.00 234.0642
 0.00 4     2.000 211     1.000 732     2.000 330   -2.000    2
2117324 Cr2OH2SO42     0.0000    17.9288                0.00 0.00 0.00 330.1218
 0.00 4     2.000 211     2.000 732     2.000 330   -2.000    2
2123300 HCrO4 -        0.9000     6.5089                -1.000.00 0.00 117.0015
 0.00 2     1.000 212     1.000 330
2123301 H2CrO4 AQ      0.0000     5.6513                0.00 0.00 0.00 118.0094
 0.00 2     1.000 212     2.000 330
2123302 Cr2O7 -2      -2.9950    14.5571                -2.000.00 0.00 215.9878
 0.00 3     2.000 212     2.000 330    -1.000    2
2121800 CrO3CL -       0.0000     7.3086                -1.000.00 0.00 135.4472
 0.00 4     1.000 212     1.000 180     2.000 330   -1.000    2
2125800 CrO3H2PO4-     0.0000    29.3634                -1.000.00 0.00 196.9814
 0.00 4     1.000 212     4.000 330     1.000 580   -1.000    2
2125801 CrO3HPO4-2     0.0000    26.6806                -2.000.00 0.00 195.9735
 0.00 4     1.000 212     3.000 330     1.000 580   -1.000    2
2127320 CrO3SO4-2      0.0000     8.9937                -2.000.00 0.00 196.0518
 0.00 4     1.000 212     1.000 732     2.000 330   -1.000    2
5002120 NACrO4-        0.0000     0.6963                -1.000.00 0.00 138.9834
 0.00 2     1.000 212     1.000 500
4102120 KCrO4-         0.0000     0.7990                -1.000.00 0.00 155.0919
 0.00 2     1.000 212     1.000 410
3300020 K OH-       13.345    -13.998                    -1. 3.5  0.0 17.0074
      2     1.000   2    -1.000 330
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3307700 KH3SI04 -   8.9350    -9.9300                    -1. 4.0  0.0 95.1070
      2    1.000 770     -1.000 330
3307701 KH2SI04 -2 29.7140    -21.6190                   -2. 5.4  0.0 94.0990
      2    1.000 770     -2.000 330
7702700 KSIF6 -2    -16.2600  30.1800                    -2. 5.0  0.0 142.0760
      4    1.000 770      6.000 270     4.000 330    -4.000   2
3300900 KH2B03 -1   3.2240    -9.2400                    -1. 2.5  0.0 60.8250
      2    1.000  90     -1.000 330
0902700 KBF(OH)3 -  1.8500    -0.3990                    -1. 2.5  0.0 80.8310
      2    1.000  90      1.000 270
0902701 KBF2(OH)2 - 1.63500   7.63000                    -1. 2.5  0.0 82.8220
      4    1.000  90      2.000 270    -1.000   2     1.000 330
0902702 KBF3OH -    -1.5800   13.66700                   -1. 2.5  0.0 84.8130
      4    1.000  90      3.000 270    -2.000   2     2.000 330
0902703 KBF4 -      -1.7950   20.27400                   -1. 2.5  0.0 86.8040
      4    1.000  90      4.000 270    -3.000   2     3.000 330
3304900 KNH3 AQ     12.4800   -9.2520                     0. 0.0  0.0 17.0300
      2    1.000 490     -1.000 330
4907320 KNH4SO4 -   0.0000     1.1100                    -1. 5.0  0.0 114.1000
      2    1.000 490      1.000 732
4603300 KMGOH +     15.935     -11.79                     1. 6.5  0.0 41.3190
      3    1.000 460      1.000   2    -1.000 330
4602700 KMGF +      4.6740     1.8200                     1. 4.5  0.0 43.3100
      2    1.000 460      1.000 270
4601400 KMGCO3 AQ   2.0220     2.9800                     0. 0.0  0.0 84.3210
 2.00 2    1.000 460      1.000 140
4601401 KMGHCO3 +   -2.430     11.400                     1. 4.0  0.0 85.3290
 1.00 3    1.000 460      1.000 140     1.000 330
4607320 KMGSO4 AQ   1.3990     2.2500                     0. 0.0  0.0 120.3730
      2    1.000 460      1.000 732
4605800 KMGPO4 -    3.1000     6.5890                    -1. 5.4  0.0 119.2830
      2    1.000 460      1.000 580
4605801 KMGH2PO4 +  -1.120     21.066                     1. 5.4  0.0 121.2990
      3    1.000 460      1.000 580     2.000 330
4605802 KMGHPO4 AQ -0.230      15.220                     0. 0.0  0.0 120.2910
      3    1.000 460      1.000 580     1.000 330
1503300 KCAOH +     14.535    -12.598                     1. 6.0  0.0 57.0870
      3    1.000 150      1.000   2    -1.000 330
1501400 KCAHCO3 +   1.7900     11.330                     1. 6.0  0.0 101.0970
 1.00 3    1.000 150      1.000 140     1.000 330
1501401 KCACO3 AQ   4.0300     3.1500                     0. 0.0  0.0 100.0890
 2.00 2    1.000 150      1.000 140
1507320 KCASO4 AQ   1.4700     2.3090                     0. 0.0  0.0 136.1410
      2    1.000 150      1.000 732
1505800 KCAHPO4 AQ -0.230      15.085                     0. 0.0  0.0 136.0590
      3    1.000 150      1.000 580     1.000 330
1505801 KCAPO4 -    3.1000     6.4590                    -1. 5.4  0.0 135.0510
      2    1.000 150      1.000 580
1505802 KCAH2PO4 +  -1.120     20.960                     1. 5.4  0.0 137.0670
      3    1.000 150      1.000 580     2.000 330
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1502700 KCAF +      3.7980    0.9400                            1. 5.0  0   59.0780
      2     1.000 150     1.000 270
5001400 KNACO3 -    8.9110    1.2680                           -1. 5.4  0.0 82.9990
 2.00 2     1.000 500     1.000 140
5001401 KNAHCO3 AQ  0.0000    10.0800                           0. 0.0  0.0 84.0070
 1.00 3     1.000 500     1.000 140     1.000 330
5007320 KNASO4 -    1.1200    0.7000                           -1. 5.4  0.0 119.0510
      2     1.000 500     1.000 732
5005800 KNAHPO4 -   0.0000    12.636                           -1. 5.4  0.0 118.9690
      3     1.000 500     1.000 580     1.000 330
5002700 KNAF AQ     0.0000    -0.7900                           0. 0.0  0.0 41.9880
      2     1.000 500     1.000 270
4107320 KKSO4 -     2.2500    0.8500                           -1. 5.4  0.0 135.1630
      2     1.000 410     1.000 732
4105800 KKHPO4 -    0.0000    12.640                           -1. 5.4  0.0 135.0810
      3     1.000 410     1.000 580     1.000 330
0303300 KALOH +2    11.8990   -4.9900                           2. 5.4  0.0 43.9880
      3     1.000  30     1.000   2    -1.000 330
0303301 KAL(OH)2 +  0.0000    -10.1000                          1. 5.4  0.0 60.9960
      3     1.000  30     2.000   2    -2.000 330
0303302 KAL(OH)4 -  44.0600   -23.0000                         -1. 4.5  0.0 95.0110
      3     1.000  30     4.000   2    -4.000 330
0302700 KALF +2     0.0000    7.0100                            2. 5.4  0.0 45.9790
      2     1.000  30     1.000 270
0302701 KALF2 +     20.0000   12.7500                           1. 5.4  0.0 64.9780
      2     1.000  30     2.000 270
0302702 KALF3 AQ    2.5000    17.0200                           0. 0.0  0.0 83.9760
      2     1.000  30     3.000 270
0302703 KALF4 -     0.0000    19.7200                          -1. 4.5  0.0 102.9750
      2     1.000  30     4.000 270
0307320 KALSO4 +    2.1500    3.0200                            1. 4.5  0.0 123.0430
      2     1.000  30     1.000 732
0307321 KAL(SO4)2 - 2.8400    4.9200                           -1. 4.5  0.0 219.1040
      2     1.000  30     2.000 732
0303303 KAL(OH)3 AQ 0.0000    -16.0000                          0. 0.0  0.0 78.0030
      3     1.000  30     3.000   2    -3.000 330
2803300 KFEOH +     13.1990   -9.5000                           1. 5.0  0.0 72.8540
      3     1.000 280     1.000   2    -1.000 330
2803301 KFEOH3 -1   30.3000   -31.0000                         -1. 5.0  0.0 106.8690
      3     1.000 280     3.000   2    -3.000 330
2807320 KFESO4 AQ   3.2300    2.2500                            0. 0.0  0.0 151.9080
      2     1.000 280     1.000 732
2805800 KFEH2PO4 +  0.0000    22.253                            1. 5.4  0.0 152.8340
      3     1.000 280     1.000 580     2.000 330
2803302 KFEOH2 AQ   28.5650   -20.5700                          0. 0.0  0.0 89.8610
      3     1.000 280     2.000   2    -2.000 330
2805801 KFEHPO4 AQ  0.0000    15.950                            0. 0.0  0.0 151.8260
      3     1.000 280     1.000 580     1.000 330
2807300 KFE(HS)2 AQ 0.0000    8.9500                            0. 0.0  0.0 121.9900
      2     1.000 280     2.000 730
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2807301 KFE(HS)3 -  0.0000    10.9870                             -1. 0.0   0.0 155.0620
      2     1.000 280      3.000 730
2813300 KFEOH +2    10.3990   -2.1900                              2. 5.0   0.0 72.8540
      3     1.000 281      1.000   2     -1.000 330
2815800 KFEHPO4 +   -7.300    17.780                               1. 5.4   0.0 151.8260
      3     1.000 281      1.000 580      1.000 330
2817320 KFESO4 +    3.9100    3.9200                               1. 5.0   0.0 151.9080
      2     1.000 281      1.000 732
2811800 KFECL +2    5.6000    1.4800                               2. 5.0   0.0 91.3000
      2     1.000 281      1.000 180
2811801 KFECL2 +    0.0000    2.1300                               1. 5.0   0.0 126.7530
      2     1.000 281      2.000 180
2811802 KFECL3 AQ   0.0000    1.1300                               0. 0.0   0.0 162.2060
      2     1.000 281      3.000 180
2813301 KFEOH2 +    0.0000   -5.6700                               1. 5.4   0.0 89.8610
      3     1.000 281      2.000   2     -2.000 330
2813302 KFEOH3 AQ   0.0000   -13.6000                              0. 0.0   0.0 106.8690
      3     1.000 281      3.000   2     -3.000 330
2813303 KFEOH4 -    0.0000   -21.6000                             -1. 5.4   0.0 123.8760
      3     1.000 281      4.000   2     -4.000 330
2815801 KFEH2PO4 +2 0.0000    24.980                               2. 5.4   0.0 152.8340
      3     1.000 281      1.000 580      2.000 330
2812700 KFEF +2     2.6990    6.1990                               2. 5.0   0.0 74.8450
      2     1.000 281      1.000 270
2812701 KFEF2 +     4.8000    10.8000                              1. 5.0   0.0 93.8430
      2     1.000 281      2.000 270
2812702 KFEF3 AQ    5.3990    14.000                               0. 0.0   0.0 112.8420
      2     1.000 281      3.000 270
2817321 KFE(SO4)2 - 4.6000    5.4200                              -1. 0.0   0.0 247.9700
      2     1.000 281      2.000 732
2811410 KFE FULVATE 0.0000    9.3990                               1. 0.0   0.0 705.8470
      2     1.000 281      1.000 141
2811420 KFE HUMATE  0.0000    9.3990                               1. 0.0   0.0 2055.8460
      2     1.000 281      1.000 142
2813304 KFE2(OH)2+4 13.5000   -2.9500                              4. 0.0   0.0 145.7080
      3     2.000 281      2.000   2     -2.000 330
2813305 KFE3(OH)4+5 14.3000   -6.3000                              5. 0.0   0.0 235.5700
      3     3.000 281      4.000   2     -4.000 330
4407320 K..ISO4 -   0.0000    0.6400                              -1. 5.0   0.0 103.0000
      2     1.000 440      1.000 732
8003300 KSROH +     14.495    -13.178                              1. 5.0   0.0 104.6270
      3     1.000 800      1.000   2     -1.000 330
1003300 KBAOH +     15.095    -13.358                              1. 5.0   0.0 154.3470
      3     1.000 100      1.000   2     -1.000 330
4701800 KMNCL +     0.0000    0.6070                               1. 5.0   0.0 90.3910
      2     1.000 470      1.000 180
4701801 KMNCL2 AQ   0.0000    0.0410                               0. 0.0   0.0 125.8440
      2     1.000 470      2.000 180
4701802 KMNCL3 -    0.0000    -.30500                             -1. 5.0   0.0 161.2970
      2     1.000 470      3.000 180
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4703300 KMNOH +     14.3990    -10.5900                   1. 5.0  0.0 161.2970
      3     1.000 470     1.000   2    -1.000 330
4703301 KMN(OH)3 -1 0.0000     -34.8000                  -1. 5.0  0.0 105.9600
      3     1.000 470     3.000   2    -3.000 330
4702700 KMNF +      0.0000     0.8500                     1. 5.0  0.0 73.9360
      2     1.000 470     1.000 270
4707320 KMNSO4 AQ   2.1700     2.2600                     0. 0.0  0.0 150.9990
      2     1.000 470     1.000 732
4701400 KMNHCO3 +   0.0000     11.600                     1. 5.0  0.0 115.9550
 1.00 3     1.000 470     1.000 140      1.000 330
2301800 KCUCL2 -    -0.42      5.5                       -1. 4.0  0.0 134.452
      2     1.000 230     2.000 180
2301801 KCUCL3 -2     0.26     5.70                      -2. 5.0  0.0 169.905
      2     1.000 230     3.000 180
2307300 KCU(S4)2 -3 0.0        3.39                      -3. 23.0 0.0 320.058
      4     1.000 230     2.000 730      6.000 731      -2.000 330
2307301 KCUS4S5 -3  0.0        2.66                      -3. 25.0 0.0 352.122
      4     1.000 230     2.000 730      7.000 731      -2.000 330
2311400 KCUCO3 AQ   0.0000     6.7300                     0. 0.0  0.0 123.5550
 2.00 2     1.000 231     1.000 140
2311401 KCU(CO3)2-2 0.0000     9.8300                    -2. 0.0  0.0 183.5640
 4.00 2     1.000 231     2.000 140
2311800 KCUCL +     8.6500     0.4300                     1. 4.0  0.0 98.9990
      2     1.000 231     1.000 180
2311801 KCUCL2 AQ   10.5600    0.1600                     0. 0.0  0.0 134.4520
      2     1.000 231     2.000 180
2311802 KCUCL3 -    13.6900    -2.2900                   -1. 4.0  0.0 169.9050
      2     1.000 231     3.000 180
2311803 KCUCL4 -2   17.7800    -4.5900                   -2. 5.0  0.0 205.3580
      2     1.000 231     4.000 180
2312700 KCUF +      1.6200     1.2600                     1. 0.0  0.0 82.5440
      2     1.000 231     1.000 270
2313300 KCUOH +     0.0000     -8.0000                    1. 4.0  0.0 80.5530
      3     1.000 231     1.000   2    -1.000 330
2313301 KCU(OH)2 AQ 0.0000     -13.6800                   0. 0.0  0.0 97.5600
      3     1.000 231     2.000   2    -2.000 330
2313302 KCU(OH)3 -  0.0000     -26.8990                  -1. 0.0  0.0 114.5680
      3     1.000 231     3.000   2    -3.000 330
2313303 KCU(OH)4 -2 0.0000     -39.6000                  -2. 0.0  0.0 131.5750
      3     1.000 231     4.000   2    -4.000 330
2313304 KCU2(OH)2+2 17.5390    -10.3590                   2. 0.0  0.0 161.1060
      3     2.000 231     2.000   2    -2.000 330
2317320 KCUSO4 AQ   1.2200     2.3100                     0. 0.0  0.0 159.6070
      2     1.000 231     1.000 732
2317300 KCU(HS)3 -  0.0000     25.8990                   -1. 0.0  0.0 162.7610
      2     1.000 231     3.000 730
2311402 KCUHCO3 +   0.0000     13.000                     1. 0.0  0.0 124.5630
 1.00 3     1.000 231     1.000 140      1.000 330
2311410 KCU FULVATE 0.0000     6.1990                     0. 0.0  0.0 713.5460
      2     1.000 231     1.000 141
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2311420 KCU HUMATE  0.0000   6.1990                      0. 0.0  0.0 2063.5450
      2   1.000 231      1.000 142
9501800 KZNCL +     7.7900   0.4300                      1. 4.0  0.0 100.8230
      2   1.000 950      1.000 180
9501801 KZNCL2 AQ   8.5000   0.4500                      0. 0.0  0.0 136.2760
      2   1.000 950      2.000 180
9501802 KZNCL3 -    9.5600   0.5000                     -1. 4.0  0.0 171.7290
      2   1.000 950      3.000 180
9501803 KZNCL4 -2  10.9600   0.1990                     -2. 5.0  0.0 207.1820
      2   1.000 950      4.000 180
9502700 KZNF +      2.2200   1.1500                      1. 0.0  0.0 84.3680
      2   1.000 950      1.000 270
9503300 KZNOH +    13.3990  -8.9600                      1. 0.0  0.0 82.3770
      3   1.000 950      1.000   2    -1.000 330
9503301 KZN(OH)2 AQ 0.0000  -16.8990                     0. 0.0  0.0 99.3840
      3   1.000 950      2.000   2    -2.000 330
9503302 KZN(OH)3 -  0.0000  -28.3990                    -1. 0.0  0.0 116.3920
      3   1.000 950      3.000   2    -3.000 330
9503303 KZN(OH)4 -2 0.0000  -41.1990                    -2. 0.0  0.0 133.3990
      3   1.000 950      4.000   2    -4.000 330
9501804 KZNOHCL AQ  0.0000  -7.4800                      0. 0.0  0.0 117.8300
      4   1.000 950      1.000   2    -1.000 330     1.000 180
9507300 KZN(HS)2 AQ 0.0000   14.9400                     0. 0.0  0.0 131.5130
      2   1.000 950      2.000 730
9507301 KZN(HS)3 -  0.0000   16.1000                    -1. 0.0  0.0 164.5850
      2   1.000 950      3.000 730
9507320 KZNSO4 AQ   1.3600   2.3700                      0. 0.0  0.0 161.4310
      2   1.000 950      1.000 732
9507321 KZN(SO4)2-2 0.0000   3.2800                     -2. 0.0  0.0 257.4930
      2   1.000 950      2.000 732
9501300 KZNBR +     0.0000  -0.5800                      1. 0.0  0.0 145.2740
      2   1.000 950      1.000 130
9501301 KZNBR2 AQ   0.0000  -0.9800                      0. 0.0  0.0 225.1780
      2   1.000 950      2.000 130
9503800 KZNI +      0.0000  -2.9100                      1. 0.0  0.0 192.2740
      2   1.000 950      1.000 380
9503801 KZNI2 AQ    0.0000  -1.6900                      0. 0.0  0.0 319.1780
      2   1.000 950      2.000 380
9501400 KZNHCO3 +   0.0000   12.400                      1. 0.0  0.0 126.3570
 1.00 3   1.000 950      1.000 140     1.000 330
9501401 KZNCO3 AQ   0.0000   5.3000                      0. 0.0  0.0 125.3790
 2.00 2   1.000 950      1.000 140
9501402 KZN(CO3)2-2 0.0000   9.6300                     -2. 0.0  0.0 185.3580
 4.00 2   1.000 950      2.000 140
1601800 KCDCL +     0.5900   1.9800                      1. 0.0  0.0 147.8530
      2   1.000 160      1.000 180
1601801 KCDCL2 AQ   1.2400   2.6000                      0. 0.0  0.0 183.3060
      2   1.000 160      2.000 180
1601802 KCDCL3 -    3.9000   2.3990                     -1. 0.0  0.0 218.7590
      2   1.000 160      3.000 180
1602700 KCDF +      0.0000   1.1000                      1. 0.0  0.0 131.3980
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      2     1.000 160     1.000 270
1602701 KCDF2 AQ    0.0000    1.5000                      0. 0.0  0.0 150.3960
      2     1.000 160     2.000 270
1601402 KCD(CO3)3-4 0.0000    6.2200                     -4. 0.0  0.0 292.4280
 6.00 2     1.000 160     3.000 140
1603300 KCDOH +     13.1000   -10.0800                    1. 0.0  0.0 129.4070
      3     1.000 160     1.000   2    -1.000 330
1603301 KCD(OH)2 AQ 0.0000    -20.3500                    0. 0.0  0.0 146.4140
      3     1.000 160     2.000   2    -2.000 330
1603302 KCD(OH)3 -  0.0000    -33.3000                   -1. 0.0  0.0 163.4220
      3     1.000 160     3.000   2    -3.000 330
1603303 KCD(OH)4 -2 0.0000    -47.3500                   -2. 0.0  0.0 180.4290
      3     1.000 160     4.000   2    -4.000 330
1603304 KCD2OH +3   10.8990   -9.3900                     3. 0.0  0.0 241.8074
      3     2.000 160     1.000   2    -1.000 330
1601803 KCDOHCL AQ  4.3550    -7.4040                     0. 0.0  0.0 164.8600
      4     1.000 160     1.000   2    -1.000 330    1.000 180
1604920 KCDNO3 +    -5.2000   0.3990                      1. 0.0  0.0 174.4040
      2     1.000 160     1.000 492
1607320 KCDSO4 AQ   1.0800    2.4600                      0. 0.0  0.0 208.4610
      2     1.000 160     1.000 732
1607300 KCDHS +     0.0000    10.1700                     1. 0.0  0.0 145.4720
      2     1.000 160     1.000 730
1607301 KCD(HS)2 AQ 0.0000    16.5300                     0. 0.0  0.0 178.5430
      2     1.000 160     2.000 730
1607302 KCD(HS)3 -  0.0000    18.7100                    -1. 0.0  0.0 211.6150
      2     1.000 160     3.000 730
1607303 KCD(HS)4 -2 0.0000    20.9000                    -2. 0.0  0.0 244.6870
      2     1.000 160     4.000 730
1601300 KCDBR +     -0.8100   2.1700                      1. 0.0  0.0 192.3040
      2     1.000 160     1.000 130
1603800 KCDI +      -2.3700   2.1500                      1. 0.0  0.0 239.3040
      2     1.000 160     1.000 380
1603801 KCDI2 AQ    0.0000    3.5900                      0. 0.0  0.0 366.2080
      2     1.000 160     2.000 380
1601400 KCDHCO3 +   0.0000    12.400                      1. 0.0  0.0 173.4170
 1.00 3     1.000 160     1.000 140     1.000 330
1601401 KCDCO3 AQ   0.0000    5.3990                      0. 0.0  0.0 172.4090
 2.00 2     1.000 160     1.000 140
1607321 KCD(SO4)2-2 0.0000    3.5000                     -2. 0.0  0.0 208.4610
      2     1.000 160     2.000 732
1601410 KCD FULVATE 0.0000    3.5000                      0. 0.0  0.0 762.3990
      2     1.000 160     1.000 141
1601420 KCD HUMATE  0.0000    3.5000                      0. 0.0  0.0 2112.3990
      2     1.000 160     1.000 142
6001800 KPBCL +     4.3800    1.6000                      1. 0.0  0.0 242.6430
      2     1.000 600     1.000 180
6001801 KPBCL2 AQ   1.0800    1.8000                      0. 0.0  0.0 278.0960
      2     1.000 600     2.000 180
6001802 KPBCL3 -    2.1700    1.6990                     -1. 0.0  0.0 313.5490
      2     1.000 600     3.000 180
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6001803 KPBCL4 -2   3.5300     1.3800                           -2. 0.0   0.0 349.0020
      2     1.000 600     4.000 180
6001400 KPB(CO3)2-2 0.0000    10.6400                           -2. 0.0   0.0 327.2080
 4.00 2     1.000 600     2.000 140
6002700 KPBF +      0.0000     1.2500                            1. 0.0   0.0 226.1880
      2     1.000 600     1.000 270
6002701 KPBF2 AQ    0.0000     2.5600                            0. 0.0   0.0 245.1860
      2     1.000 600     2.000 270
6002702 KPBF3 -     0.0000     3.4200                           -1. 0.0   0.0 264.1850
      2     1.000 600     3.000 270
6002703 KPBF4 -2    0.0000     3.1000                           -2. 0.0   0.0 283.1830
      2     1.000 600     4.000 270
6003300 KPBOH +     0.0000    -7.7100                            1. 0.0   0.0 224.1970
      3     1.000 600     1.000   2    -1.000 330
6003301 KPB(OH)2 AQ 0.0000   -17.1200                            0. 0.0   0.0 241.2040
      3     1.000 600     2.000   2    -2.000 330
6003302 KPB(OH)3 -  0.0000   -28.0600                           -1. 0.0   0.0 258.2120
      3     1.000 600     3.000   2    -3.000 330
6003303 KPB2OH +3   0.0000    -6.3600                            3. 0.0   0.0 431.3870
      3     2.000 600     1.000   2    -1.000 330
6004920 KPBNO3 +    0.0000     1.1700                            1. 0.0   0.0 269.1940
      2     1.000 600     1.000 492
6007320 KPBSO4 AQ   0.0000     2.7500                            0. 0.0   0.0 303.2510
      2     1.000 600     1.000 732
6007300 KPB(HS)2 AQ 0.0000    15.2700                            0. 0.0   0.0 273.3330
      2     1.000 600     2.000 730
6007301 KPB(HS)3 -  0.0000    16.5700                           -1. 0.0   0.0 306.4050
      2     1.000 600     3.000 730
6003304 KPB3(OH)4+2 26.5000  -23.8800                            2. 0.0   0.0 689.5990
      3     3.000 600     4.000   2    -4.000 330
6001300 KPBBR +     2.8800     1.7700                            1. 0.0   0.0 287.0940
      2     1.000 600     1.000 130
6001301 KPBBR2 AQ   0.0000     1.4400                            0. 0.0   0.0 366.9980
      2     1.000 600     2.000 130
6003800 KPBI +      0.0000     1.9400                            1. 0.0   0.0 334.0940
      2     1.000 600     1.000 380
6003801 KPBI2 AQ    0.0000     3.1990                            0. 0.0   0.0 460.9980
      2     1.000 600     2.000 380
6001401 KPBCO3 AQ   0.0000     7.2400                            0. 0.0   0.0 267.1990
 2.00 2     1.000 600     1.000 140
6003305 KPB(OH)4 -2 0.0000   -39.6990                           -2. 0.0   0.0 375.2190
      3     1.000 600     4.000   2    -4.000 330
6007321 KPB(SO4)2-2 0.0000     3.4700                           -2. 0.0   0.0 399.3130
      2     1.000 600     2.000 732
6001402 KPBHCO3 +   0.0000    13.200                             1. 0.0   0.0 268.2070
 1.00 3     1.000 600     1.000 140     1.000 330
5401300 KNIBR +     0.0000     0.5000                            1. 0.0   0.0 138.6140
      2     1.000 540     1.000 130
5401800 KNICL +     0.0000     0.3990                            1. 0.0   0.0 94.1630
      2     1.000 540     1.000 180
5402700 KNIF +      0.0000     1.3000                            1. 0.0   0.0 77.7080
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      2     1.000 540     1.000 270
5403300 KNIOH +     12.4200   -9.8600                           1. 0.0  0.0 75.7170
      3     1.000 540     1.000   2    -1.000 330
5403301 KNI(OH)2 AQ 0.0000    -19.0000                          0. 0.0  0.0 92.7240
      3     1.000 540     2.000   2    -2.000 330
5403302 KNI(OH)3 -  0.0000    -30.0000                         -1. 0.0  0.0 109.7320
      3     1.000 540     3.000   2    -3.000 330
5407320 KNISO4 AQ   1.5200     2.2900                           0. 0.0  0.0 154.7710
      2     1.000 540     1.000 732
5401801 KNICL2 AQ   0.0000     0.9600                           0. 0.0  0.0 129.6160
      2     1.000 540     2.000 180
5401400 KNIHCO3 +   0.0000    12.470                            1. 0.0  0.0 119.7270
 1.00 3     1.000 540     1.000 140     1.000 330
5401401 KNICO3 AQ   0.0000     6.8700                           0. 0.0  0.0 118.7190
 2.00 2     1.000 540     1.000 140
5401402 KNI(CO3)2-2 0.0000    10.1100                          -2. 0.0  0.0 178.7280
 4.00 2     1.000 540     2.000 140
5407321 KNI(SO4)2-2 0.0000     1.0200                          -2. 0.0  0.0 250.8330
      2     1.000 540     2.000 732
0201300 KAGBR AQ    0.0000     4.2400                           0. 0.0  0.0 187.7720
      2     1.000  20     1.000 130
0201301 KAGBR2 -    0.0000     7.2800                          -1. 0.0  0.0 267.6760
      2     1.000  20     2.000 130
0201800 KAGCL AQ   -2.6800     3.2700                           0. 0.0  0.0 143.3210
      2     1.000  20     1.000 180
0201801 KAGCL2 -   -3.9300     5.2700                          -1. 0.0  0.0 178.7740
      2     1.000  20     2.000 180
0201802 KAGCL3 -2   0.0000     5.2900                          -2. 0.0  0.0 214.2270
      2     1.000  20     3.000 180
0201803 KAGCL4 -3   0.0000     5.5100                          -3. 0.0  0.0 249.6790
      2     1.000  20     4.000 180
0202700 KAGF AQ    -2.8300     0.3600                           0. 0.0  0.0 126.8660
      2     1.000  20     1.000 270
0207300 KAGHS AQ    0.0000    14.0500                           0. 0.0  0.0 140.9390
      2     1.000  20     1.000 730
0207301 KAG(HS)2 -  0.0000    18.4500                          -1. 0.0  0.0 174.0110
      2     1.000  20     2.000 730
0203800 KAGI AQ     0.0000     6.6000                           0. 0.0  0.0 234.7720
      2     1.000  20     1.000 380
0203801 KAGI2 -     0.0000    10.6800                          -1. 0.0  0.0 361.6760
      2     1.000  20     2.000 380
0203300 KAGOH AQ    0.0000   -12.0000                           0. 0.0  0.0 124.8750
      3     1.000  20     1.000   2    -1.000 330
0203301 KAG(OH)2 -  0.0000   -24.0000                          -1. 0.0  0.0 141.8820
      3     1.000  20     2.000   2    -2.000 330
0207320 KAGSO4 -    1.4900     1.2900                          -1. 0.0  0.0 203.9290
      2     1.000  20     1.000 732
0204920 KAGNO3 AQ   0.0000    -0.2900                           0. 0.0  0.0 169.8720
      2     1.000  20     1.000 492
0204910 KAG(NO2)2 - 0.0000     2.2200                          -1. 0.0  0.0 199.8790
      2     1.000  20     2.000 491
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0201302 KAGBR3 -2   0.0000    8.7100                          -2. 0.0  0.0 347.5800
      2     1.000  20     3.000 130
0203802 KAGI3 -2    -27.0300  13.3700                         -2. 0.0  0.0 488.5810
      2     1.000  20     3.000 380
0203803 KAGI4 -3    0.0000    14.0800                         -3. 0.0  0.0 615.4850
      2     1.000  20     4.000 380
0207302 KAG(S4)2 -3 0.0000    0.9910                          -3. 22.0 0.0 364.3800
      4     1.000  20     2.000 730    -2.000 330     6.000 731
0207303 KAGS4S5 -3  0.0000    0.6800                          -3. 24.0 0.0 396.4440
      4     1.000  20     2.000 730    -2.000 330     7.000 731
0207304 KAG(HS)S4-2 0.0000    10.4310                         -2. 15.0 0.0 269.1960
      4     1.000  20     2.000 730    -1.000 330     3.000 731
0201410 KAG FULVATE 0.0000    2.3990                          -1. 0.0  0.0 757.8680
      2     1.000  20     1.000 141
0201420 KAG HUMATE  0.0000    2.3990                          -1. 0.0  0.0 2107.8670
      2     1.000  20     1.000 142
3300600 KH2ASO3 -   6.5600    -9.2280                         -1. 0.0  0.0 124.9350
      2     1.000  60    -1.000 330
3300601 KHASO3 -2   14.1990   -21.33                          -2. 0.0  0.0 123.9270
      2     1.000  60    -2.000 330
3300602 KASO3 -3    20.2500   -34.7440                        -3. 0.0  0.0 122.9190
      2     1.000  60    -3.000 330
3300610 KH4ASO3 +   0.0000    -0.3050                          1. 0.0  0.0 126.9510
      2     1.000  60     1.000 330
3300611 KH2ASO4 -   -1.6900   -2.2430                         -1. 0.0  0.0 140.9350
      2     1.000  61    -1.000 330
3300612 KHASO4 -2   -0.9200   -9.0010                         -2. 0.0  0.0 139.9270
      2     1.000  61    -2.000 330
3300613 KASO4 -3    3.4300    -20.5970                        -3. 0.0  0.0 138.9190
      2     1.000  61    -3.000 330
3301400 KHCO3 -     -3.6170   10.3300                         -1. 5.4  0.0 61.0170
 1.00 2     1.000 140     1.000 330
3301401 KH2CO3 AQ   -2.2470   16.681                           0. 0.0  0.0 62.0250
      2     1.000 140     2.000 330
3307320 KHSO4 -     4.9100    1.9870                          -1. 4.5  0.0 97.0690
      2     1.000 732     1.000 330
3302700 KHF AQ      3.4600    3.1690                           0. 0.0  0.0 20.0060
      2     1.000 270     1.000 330
3302701 KHF2 -      4.5500    3.7490                          -1. 3.5  0.0 39.0040
      2     2.000 270     1.000 330
3302702 KH2F2 AQ    0.0000    6.7680                           0. 0.0  0.0 40.0120
      2     2.000 270     2.000 330
3305800 KHPO4 -2    -3.5300   12.3460                         -2. 5.0  0.0 95.9790
      2     1.000 580     1.000 330
3305801 KH2PO4 -    -4.5200   19.5530                         -1. 5.4  0.0 96.9870
      2     1.000 580     2.000 330
3307300 KH2S AQ     -5.300    6.9940                           0. 0.0  0.0 34.0790
      2     1.000 730     1.000 330
3307301 KS -2       12.1000   -12.9180                        -2. 5.0  0.0 32.0640
      2     1.000 730    -1.000 330
3301410 KH FULVATE  0.0000    4.2700                          -1. 0.0  0.0 651.0080
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       2      1.000 141      1.000 330
3301420 KH HUMATE   0.0000     4.2700                               -1. 0.0   0.0 2001.0070
       2      1.000 142      1.000 330
8913300 KUOH +3      11.715     -0.656                               3. 0.0   0.0 255.0364
       3      1.000 891      1.000   2    -1.000 330
8913301 KU(OH)2 +2  17.730     -2.270                               2. 0.0   0.0 272.0437
       3     -2.000 330      1.000 891     2.000   2
8913302 KU(OH)3 +1  22.645     -4.935                               1. 0.0   0.0 289.0511
       3      1.000 891      3.000   2    -3.000 330
8913303 KU(OH)4 AQ  24.760     -8.498                               0. 0.0   0.0 306.0586
       3      1.000 891      4.000   2    -4.000 330
8913304 KU(OH)5 -1  27.575     -13.120                             -1. 0.0   0.0 323.0659
       3      1.000 891      5.000   2    -5.000 330
8912700 KUF +3       5.050      8.659                                3. 0.0   0.0 257.0274
       2      1.000 891      1.000 270
8912701 KUF2 +2      7.200      14.457                               2. 0.0   0.0 276.0258
       2      1.000 891      2.000 270
8912702 KUF3 +1      7.150      19.115                               1. 0.0   0.0 295.0242
       2      1.000 891      3.000 270
8912703 KUF4 AQ      4.600      23.640                               0. 0.0   0.0 314.0226
       2      1.000 891      4.000 270
8912704 KUF5 -1      4.850      25.238                              -1. 0.0   0.0 333.0210
       2      1.000 891      5.000 270
8912705 KUF6 -2      3.300      27.718                              -2. 0.0   0.0 352.0194
       2      1.000 391      6.000 270
8911800 KUCL +3      9.933      1.338                                3. 0.0   0.0 273.4820
       2      1.000 891      1.000 180
8917320 KUSO4 +2     3.700      5.461                                2. 0.0   0.0 334.0906
       2      1.000 891      1.000 732
8917321 KU(SO4)2 AQ 7.600       9.749                                0. 0.0   0.0 430.1522
       2      1.000 891      2.000 732
8915800 KUHPO4 +2    7.500      24.443                               2. 0.0   0.0 334.0084
       3      1.000 891      1.000 580     1.000 330
8915801 KU(HPO4)2AQ 1.700       46.833                               0. 0.0   0.0 429.9877
       3      1.000 891      2.000 580     2.000 330
8915802 KU(HPO4)3-2 -7.800      67.564                              -2. 0.0   0.0 525.9671
       3      1.000 891      3.000 580     3.000 330
8915803 KU(HPO4)4-4 -26.500     88.483                              -4. 0.0   0.0 621.9465
       3      1.000 891      4.000 580     4.000 330
8933300 KUO2OH +1   10.216     -5.090                                1. 0.0   0.0 287.0352
       3      1.000 893      1.000   2    -1.000 330
8933301 KUO2)2OH2+2 10.230     -5.645                                2. 0.0   0.0 574.0703
       3      2.000 893      2.000   2    -2.000 330
8933302 KUO2)3OH5+1 25.075     -15.593                               1. 0.0   0.0 895.1203
       3      3.000 893      5.000   2    -5.000 330
8931400 KUO2CO3 AQ  0.840      10.071                               0. 0.0   0.0 330.0372 2.00
       2      1.000 893      1.000 140
8931401 KUO2CO3)2-2 3.480      17.008                              -2. 0.0   0.0 390.0465 4.00
       2      1.000 893      2.000 140
8931402 KUO2CO3)3-4 -8.780     21.384                              -4. 0.0   0.0 450.0559 6.00
       2      1.000 893      3.000 140
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8932700 KUO2F +1     -0.450    5.105                     1. 0.0  0.0 289.0262
      2     1.000 893     1.000 270
8932701 KUO2F2 AQ    -0.900    8.920                     0. 0.0  0.0 308.0246
      2     1.000 893     2.000 270
8932702 KUO2F3 -1    -0.850   11.364                    -1. 0.0  0.0 327.0230
      2     1.000 893     3.000 270
8932703 KUO2F4 -2    -1.100   12.607                    -2. 0.0  0.0 346.0214
      2     1.000 893     4.000 270
8931800 KUO2CL +1    1.233     0.220                     1. 0.0  0.0 305.4808
      2     1.000 893     1.000 180
8937320 KUO2SO4 AQ   5.100     2.709                     0. 0.0  0.0 366.0894
      2     1.000 893     1.000 732
8937321 KUO2SO4)2-2 6.100      4.183                    -2. 0.0  0.0 462.1510
      2     1.000 893     2.000 732
8935800 KUO2HPO4 AQ -2.100    20.814                     0. 0.0  0.0 366.0072
      3     1.000 893     1.000 580     1.000 330
8935801 KUO2HPO4)2  -11.399   42.988                    -2. 0.0  0.0 461.9865
      3     1.000 893     2.000 580     2.000 330
8935802 KUO2H2PO4+1 -3.700    22.643                     1. 0.0  0.0 367.0151
      3     1.000 893     1.000 580     2.000 330
8935803 KUO2H2PO4)2 -16.5     44.70                      0. 0    0   464.002
      3     1.000 893     2.000 580     4.000 330
8935804 KUO2H2PO4)3 -28.6     66.245                    -1. 0    0   560.989
      3     1.000 893     3.000 580     6.000 330
8937700 KUO2H3SIO4            -2.4                       1. 0    0   365.135
      3     1.000 893     1.000 770    -1.000 330
7317300 KS2 -2        11.4    -14.528                   -2. 0.0  0.0  64.128
      3     1.000 730     1.000 731    -1.000 330
7317301 KS3 -2        10.4    -13.282                   -2. 0.0  0.0  96.192
      3     1.000 730     2.000 731    -1.000 330
7317302 KS4 -2         9.7     -9.829                   -2. 0.0  0.0 128.236
      3     1.000 730     3.000 731    -1.000 330
7317303 KS5 -2         9.3     -9.595                   -2. 0.0  0.0 160.320
      3     1.000 730     4.000 731    -1.000 330
7317304 KS6 -2                 -9.881                   -2. 0.0  0.0 192.384
      3     1.000 730     5.000 731    -1.000 330
9003300 VOH +                  -5.64                     1.             67.947
      3     1.000 900     1.000   2    -1.000 330
9013300 VOH +2         9.35    -2.30                     2.             67.947
      3     1.000 901     1.000   2    -1.000 330
9013301 V(OH)2 +1              -5.83                     1.             84.955
      3     1.000 901     2.000   2    -2.000 330
9013302 V(OH)3 AQ             -11.02                     0.            101.962
      3     1.000 901     3.000   2    -3.000 330
9017320 VSO4 +1                 1.44                     1.            146.998
      2     1.000 901     1.000 732
9013303 V2(OH)3 +3             -7.50                     3.            152.902
      3     2.000 901     3.000   2    -3.000 330
9013304 V2(OH)2 +4             -3.75                     4.            135.895
      3     2.000 901     2.000   2    -2.000 330
9023300 V(OH)3 +1              -5.67                     1.            101.962
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      3     1.000 902     2.000   2    -1.000 330
9023301 H2V2O4 +2             -6.44                       2.          167.894
      3     2.000 902     2.000   2    -2.000 330
9022700 VOF +         1.9      3.34                       1.           85.937
      2     1.000 902     1.000 270
9022701 VOF2 AQ      3.50      5.74                       0.          104.935
      2     1.000 902     2.000 270
9022702 VOF3 -1      4.90      7.30                      -1.          123.933
      2     1.000 902     3.000 270
9022703 VOF4 -2      6.40      8.11                      -2.          142.931
      2     1.000 902     4.000 270
9027320 VOSO4 AQ     3.72      2.45                       0.          162.997
      2     1.000 902     1.000 732
9021800 VOCL +1                0.02                       1.          102.392
      2     1.000 902     1.000 180
9033300 H3VO4 AQ    10.63     -3.30                       0.          117.962
      3     1.000 903     2.000   2    -1.000 330
9033301 H2VO4 -1    11.33     -7.09                      -1.          116.954
      3     1.000 903     2.000   2    -2.000 330
9033302 HVO4 -2     14.93    -15.15                      -2.          115.946
      3     1.000 903     2.000   2    -3.000 330
9033303 VO4 -3      19.53    -28.40                      -3.          114.938
      3     1.000 903     2.000   2    -4.000 330
9030020 V2O7 -4              -29.08                      -4.          213.876
      3     2.000 903     3.000   2    -6.000 330
9030021 HV2O7 -3             -16.32                      -3.          214.884
      3     2.000 903     3.000   2    -5.000 330
9030022 H3V2O7 -1             -3.79                      -1.          216.900
      3     2.000 903     3.000   2    -3.000 330
9030023 V3O9 -3              -15.88                      -3.          296.815
      3     3.000 903     3.000   2    -6.000 330
9030024 V4O12 -4             -20.79                      -4.          395.753
      3     4.000 903     4.000   2    -8.000 330
9030025 V10O28 -6            -17.53                      -6.          957.383
      3    10.000 903     8.000   2   -16.000 330
9030026 HV10O28 -5 21.52     -11.35                      -5.          958.391
      3    10.000 903     8.000   2   -15.000 330
9030027 H2V10O28 -4           -7.71                      -4.          959.399
      3    10.000 903     8.000   2   -14.000 330
9032700 VO2F AQ                3.12                       0.          101.937
      2     1.000 903     1.000 270
9032701 VO2F2 -1               5.67                      -1.          120.935
      2     1.000 903     2.000 270
9032702 VO2F3 -2               6.97                      -2.          139.933
      2     1.000 903     3.000 270
9032703 VO2F4 -3               7.07                      -3.          158.931
      2     1.000 903     4.000 270
9037320 VO2SO4 -1              1.71                      -1.          178.996
      2     1.000 903     1.000 732
9034920 VO2NO3 AQ             -0.43                       0.          144.944
      2     1.000 903     1.000 492
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4803300 MOO2 +2              8.61                           2.            127.94
      3     1.000 480   -2.000 002     4.000 330
4803301 MOO2(OH) +1          8.16                           1.            144.95
      3     1.000 480    3.000 330    -1.000 002
4803302 H2MOO4 AQ            8.20                           0.            161.95
      2     1.000 480    2.000 330
4803303 HMOO4 -1             4.19                          -1.            160.95
      2     1.000 480    1.000 330
8503300 TH(OH) +3           -3.80                           3.
      3    -1.000 330    1.000 850     1.000 002
8503301 TH(OH)2 +2          -6.73                           2.
      3    -2.000 330    1.000 850     2.000 002
8503302 TH2(OH)2+6          -3.94                           6.
      3    -2.000 330    2.000 850     2.000 002
8502700 THF +3               7.52                           3.
      2     1.000 850    1.000 270
8502701 THF2 +2             13.21                           2.
      2     1.000 850    2.000 270
8502702 THF3 +1             17.36                           1.
      2     1.000 850    3.000 270
8502703 THF4 AQ             20.19                           0.
      2     1.000 850    4.000 270
8501800 THCL +3              1.11                           3.
      2     1.000 850    1.000 180
8501801 THCL2 +2             0.76                           2.
      2     1.000 850    2.000 180
8501802 THCL3 +1             1.66                           1.
      2     1.000 850    3.000 180
8507320 THSO4 +2             5.45                           2.
      2     1.000 850    1.000 732
8507321 TH(SO4)3-2          10.47                          -2.
      2     1.000 850    3.000 732
8507322 TH(SO4)4-4           8.44                          -4.
      2     1.000 850    4.000 732
8504920 THNO3 +3             1.17                           3.
      2     1.000 850    1.000 492
8504921 TH(NO3)2+2           1.96                           2.
      2     1.000 850    2.000 492
8505800 THH2PO4 +3          24.19                           3.
      3     1.000 850    1.000 580     2.000 330
8505801 TH(H2PO4)2+2        48.01                           2.
      3     1.000 850    2.000 580     4.000 330
8503303 TH(OH)3 +1         -11.70                           1.
      3    -3.000 330    1.000 850     3.000 002
8503304 TH(OH)4 AQ         -15.90                           0.
      3    -4.000 330    1.000 850     4.000 002
8503305 TH4(OH)8+8         -21.03                           8.
      3    -8.000 330    4.000 850     8.000 002
8503306 TH6OH)15+9         -36.76                           9.
      3   -15.000 330    6.000 850    15.000 002
8503307 TH(OH)5 -1         -21.81                          -1.
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      3    -5.000 330      1.000 850      5.000 002
8503308 TH(OH)6 -2               -35.80                      -2.
      3    -6.000 330      1.000 850      6.000 002
8501803 THCL4 AQ                   1.16                          0.
      2     1.000 850      4.000 180
9903300 SO-                      -10.7
      3     1.000 990      -1.00 330      -1.00 992
9903301 SOH2+                      5.10
      3     1.000 990      1.000 330      1.000 992
9905000 SO-NA                     -9.00
      5     1.000 990      1.000 500      -1.00 330      -1.00 992      1.000 993
9904920 SOH2-NO3                   6.90
      5     1.000 990      1.000 330      1.000 492      1.000 992      -1.00 993
9907320 SOH2-SO4                   9.90
      5     1.000 990      1.000 732      1.000 330      1.000 992      -2.00 993
9907321 SOH2-HSO4                 15.9
      5     1.000 990      1.000 732      2.000 330      -1.00 993      1.000 992
9904100 SO-K                      -8.40
      5     1.000 990      1.000 410      -1.00 330      -1.00 992      1.000 993
9904600 SO-MG+                    -5.45
      5     1.000 990      1.000 460      -1.00 330      -1.00 992      2.000 993
9904601 SO-MGOH                  -14.25
      6     1.000 990      1.000 460       1.000 002     -2.00 330     -1.00 992 1.000 993
9901500 SO-CA+                    -5.00
      5     1.000 990      1.000 150      -1.00 330      -1.00 992      2.000 993
9901501 SO-CAOH                  -14.50
      6     1.000 990      1.000 150      1.000 002      -2.00 330     -1.00 992 1.000 993
9901800 SOH2-CL                    7.000
      5     1.000 990      1.000 180      1.000 330      1.000 992      -1.00 993
2089100 URANINITE         18.630 4.700     .000            .000         270.0278
      3    -4.000 330      1.000 891      2.000   2
2089101 UO2  (AM)         26.230 -.934     .000            .000         270.0278
      3    -4.000 330      1.000 891      2.000   2
3089100 U4O9 (C)         101.23  3.384     .000          -3.080        1096.1106
      4   -18.000 330     -2.000   1      4.000 891      9.000    2
3089101 U3O8 (C)         116.020 -21.107  .000          -34.589         842.0822
      4   -16.000 330     -4.000   1      3.000 891      8.000    2
8089100 USIO4 (C)         14.548          7.620 .000       .000         330.1121
      3    -4.000 330      1.000 891      1.000 770
4289100 UF4  (C)          18.900         18.606 .000       .000         314.0226
      2     1.000 891      4.000 270
4289101 UF4.2.5H2O          .588         27.570 .000       .000         359.0606
      3     1.000 891      4.000 270      2.500   2
7089100 UHPO4)2,4H2O      -3.840         51.584 .000       .000         502.0486
      4     1.000 891      2.000 580      2.000 330      4.000    2
7015000 NINGYOITE          2.270         53.906 .000       .000         504.0822
      4     1.000 891      1.000 150      2.000 580      2.000    2
2089300 UO3 (C)           19.315 -7.719     .000           .000         286.0272
      3    -2.000 330      1.000 893      1.000   2
2089301 GUMMITE           23.015 -10.403    .000           .000         286.0272
      3    -2.000 330      1.000 893      1.000   2
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2089302 B-U02(OH)2      13.730    -5.544    .000    .000               304.0424
      3     -2.000 330   1.000 893      2.000   2
2089303 SCHOEPITE       12.045    -5.404    .000    .000               322.0576
      3     -2.000 330   1.000 893      3.000   2
5089300 RUTHERFORDIN     1.440    14.439    .000    .000               330.0370
      2      1.000 893   1.000 140
7089300 (U02)3(P04)2   -94.900    49.037 129.134    .000              1000.0262
      2      3.000 893   2.000 580
7089301 H-AUTUNITE       3.600    47.931    .000    .000               732.0144
      3      2.000 330   2.000 893      2.000 580
7050000 NA-AUTUNITE       .460    47.409    .000    .000               775.9780
      3      2.000 500   2.000 893      2.000 580
7041000 K-AUTUNITE      -5.860    48.244    .000    .000               808.2024
      3      2.000 410   2.000 893      2.000 580
7049000 URAMPHITE       -9.700    51.749    .000    .000               766.0756
      3      2.000 893   2.000 490      2.000 580
7046000 SALEEITE        20.180    43.646    .000    .000               754.3104
      3      2.000 893   1.000 460      2.000 580
7015001 AUTUNITE        14.340    43.927    .000    .000               770.0784
      3      2.000 893   1.000 150      2.000 580
7080000 SR-AUTUNITE     13.050    44.457    .000    .000               817.6184
      3      2.000 893   1.000 800      2.000 580
7010000 URANOCIRCITE    10.100    44.631    .000    .000               867.3384
      3      2.000 893   1.000 100      2.000 580
7028000 BASSETITE       19.900    44.485    .000    .000               785.8454
      3      2.000 893   1.000 280      2.000 580
7023102 TORBERNITE      15.900    45.279    .000    .000               793.5444
      3      2.000 893   1.000 231      2.000 580
7060000 PRZHEVALSKIT    11.000    44.365    .000    .000               937.1883
      3      2.000 893   1.000 600      2.000 580
8015000 URANOPHANE        .000   -17.490    .000    .000               766.5176
      4     -6.000 330   2.000 893      1.000 150      2.000 770
5189300 U02N03)2        20.140   -12.369    .000    .000               394.0380
      2      1.000 893   2.000 492
5189301 U02N03.2H20      6.060    -4.851    .000    .000               430.0690
      3      1.000 893   2.000 492      2.000   2
5189302 U02N03.3H20      2.405    -3.642    .000    .000               448.0840
      3      1.000 893   2.000 492      3.000   2
5189303 U02N03.6H20     -4.770    -2.300    .000    .000               502.1300
      3      1.000 893   2.000 492      6.000   2
2003000 ALOH3(A)        27.045   -10.380  -9.690    .000                78.0073
      3      1.000  30   3.000   2     -3.000 330
6003000 ALOHS04           .000     3.230   3.390   3.070               140.0505
      4     -1.000 330   1.000  30      1.000 732      1.000   2
6003001 AL4(OH)10S04      .000   -22.700    .000    .000               374.0616
      4    -10.000 330   4.000  30      1.000 732     10.000   2
6041000 ALUM K          -7.220     5.170    .000    .000               438.3597
      4      1.000 410   1.000  30      2.000 732     12.000   2
6041001 ALUNITE         -3.918     1.346    .000    .000               414.2141
      5      1.000 410   3.000  30      2.000 732      6.000   2     -6.000 330
6015000 ANHYDRITE        3.769     4.637    .000    .000               136.1416
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      2     1.000 150     1.000 732
5015000 ARAGONITE        2.615     8.360     .000    .000               100.0894
      2     1.000 150     1.000 140
5046000 ARTINITE        28.742    -9.600     .000    .000               196.6941
      4    -2.000 330     2.000 460     1.000 140     5.000   2
4210000 BAF2            -1.000     5.760    6.740   4.650               175.3368
      2     1.000 100     2.000 270
6010000 BARITE          -6.280     9.976     .000   9.773               233.4016
      2     1.000 100     1.000 732
2003001 BOEHMITE        28.130    -8.578   -8.065    .000                59.9884
      3    -3.000 330     1.000  30     2.000   2
2046000 BRUCITE         25.840   -16.792     .000    .000                58.3268
      3     1.000 460     2.000   2    -2.000 330
5015001 CALCITE          2.585     8.475    8.560    .000               100.0894
      2     1.000 150     1.000 140
6080000 CELESTITE         .470     6.465     .000   6.349               183.6816
      2     1.000 800     1.000 732
2077000 CHALCEDONY      -4.615     3.523     .000    .000                60.0848
      2    -2.000   2     1.000 770
8646000 CHRYSOTILE      52.485   -32.188     .000    .000               277.1349
      4    -6.000 330     3.000 460     2.000 770     1.000   2
8246000 CLINOENSTITE    20.015   -11.338  -10.972 -11.632               100.3964
      4    -1.000   2     1.000 460     1.000 770    -2.000 330
2077001 CRISTOBALITE    -5.500     3.587     .000    .000                60.0848
      2    -2.000   2     1.000 770
2003002 DIASPORE        24.630    -6.873     .000    .000                59.9884
      3    -3.000 330     1.000  30     2.000   2
8215000 DIOPSIDE        32.280   -19.886     .000    .000               216.5608
      5    -2.000   2     1.000 150     1.000 460     2.000 770    -4.000 330
5015002 DOLOMITE         8.290    17.000     .000    .000               184.4108
      3     1.000 150     1.000 460     2.000 140
6046000 EPSOMITE        -2.820     2.140     .000    .000               246.4807
      3     1.000 460     1.000 732     7.000   2
8646003 SEPIOLITE(C)    27.268   -15.913     .000    .000               323.9313
      4     -.500   2     2.000 460     3.000 770    -4.000 330
2028100 FERRIHYDRITE      .000    -4.891   -1.557  -4.996               104.8692
      3    -3.000 330     1.000 281     3.000   2
2028101 FE3(OH)8          .000   -20.222  -17.112 -24.105               297.6002
      4    -8.000 330     2.000 281     1.000 280     8.000   2
4128100 FEOH)2.7CL.3      .000     3.040     .000    .000               110.4029
      4    -2.700 330     1.000 281     2.700   2      .300 180
1028000 FES PPT           .000     3.915     .000    .000                85.9110
      3    -1.000 330     1.000 280     1.000 730
6028100 FE2(SO4)3       59.120    -3.580     .650    .000               395.8788
      2     2.000 281     3.000 732
7015002 FCO3APATITE    -39.390   114.400     .000    .000               967.3670
      6     9.496 150      .360 500      .144 460     4.800 580     1.200 140      2.48 270
4215000 FLUORITE        -4.710    10.960     .000    .000                78.0768
      2     1.000 150     2.000 270
8046000 FORSTERITE      48.510   -28.298     .000    .000               236.8234
      3    -4.000 330     2.000 460     1.000 770
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2003003 GIBBSITE (C)    22.800    -8.770  -8.487  -9.140                78.0037
      3    -3.000 330     1.000  30     3.000   2
2028102 GOETHITE        14.480     -.500    .000    .000                86.8536
      3    -3.000 330     1.000 281     2.000   2
8628000 GREENALITE        .000   -20.810    .000    .000               365.7393
      4    -6.000 330     3.000 280     2.000 770     1.000   2
1028001 GREIGITE          .000    45.035    .000    .000               289.7970
      4    -4.000 330     2.000 281     1.000 280     4.000 730
6015001 GYPSUM           -.261     4.848    .000    .000               172.1722
      3     1.000 150     1.000 732     2.000   2
4150000 HALITE           -.918    -1.582    .000    .000                58.4428
      2     1.000 500     1.000 180
2028105 HEMATITE        30.845     4.008    .000    .000               155.6919
      3    -6.000 330     2.000 281     3.000   2
5015003 HUNTITE         25.760    29.968    .000    .000               353.0536
      3     3.000 460     1.000 150     4.000 140
5046001 HYDRMAGNESIT    52.210     8.766    .000    .000               467.6736
      4     5.000 460     4.000 140    -2.000 330     6.000   2
6050000 JAROSITE NA     36.180    11.200    .000    .000               478.6978
      5    -6.000 330     1.000 500     3.000 281     2.000 732      6.000  2
6041002 JAROSITE K      31.280    14.800    .000    .000               494.8100
      5    -6.000 330     1.000 410     3.000 281     2.000 732      6.000  2
6028101 JAROSITE H      55.150    12.100    .000    .000               480.7320
      4    -5.000 330     3.000 281     2.000 732     7.000   2
1028002 MACKINAWITE       .000     4.648    .000    .000                87.9110
      3    -1.000 330     1.000 280     1.000 730
8450000 MAGADIITE         .000    14.300    .000    .000               532.6521
      4    -1.000 330    -9.000   2     1.000 500     7.000 770
2028104 MAGHEMITE         .000    -6.386    .000    .000               159.6922
      3    -6.000 330     2.000 281     3.000   2
5046002 MAGNESITE        6.169     8.029   8.279   7.779                84.3214
      2     1.000 460     1.000 140
3028000 MAGNETITE       50.460    -3.737  -3.367  -6.595               231.5386
      4    -8.000 330     2.000 281     1.000 280     4.000   2
6028000 MELANTERITE     -2.860     2.470    .000    .000               278.0157
      3     1.000 280     1.000 732     7.000   2
6050001 MIRABILITE     -18.987     1.114    .000    .000               322.1942
      3     2.000 500     1.000 732    10.000   2
3050000 NATRON         -15.745     1.311    .000    .000               286.1420
      3     2.000 500     1.000 140    10.000   2
5046003 NESQUEHONITE     5.789     5.621   5.133   4.546               138.3673
      3     1.000 460     1.000 140     3.000   2
8646001 PHLOGOPITE      86.360   -66.300    .000    .000               417.2863
      5   -10.000 330     1.000 410     3.000 460     1.000  30      3.000 770
1028003 PYRITE         -11.300    18.479    .000    .000               119.9750
      4    -2.000 330    -2.000   1     1.000 280     2.000 730
2077002 QUARTZ          -6.220     4.006    .000    .000                60.0848
      2    -2.000   2     1.000 770
8646004 SEPIOLITE(A)      .000   -18.780    .000    .000               323.9308
      4     -.500   2     2.000 460     3.000 770    -4.000 330
5028000 SIDERITE         5.328    10.550  12.104    .000               115.8564
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      2     1.000 280     1.000 140
2077003 SIO2(A,GL)      -4.440     3.018    .000    .000                60.0848
      2    -2.000   2     1.000 770
2077004 SIO2(A,PT)      -3.910     2.710    .000    .000                60.0848
      2    -2.000   2     1.000 770
4280000 SRF2            -1.250     8.540   9.120    .000               125.6168
      2     1.000 800     2.000 270
7028100 STRENGITE        2.030    26.400  29.123  26.235               186.8490
      3     1.000 281     1.000 580     2.000   2
5080000 STRONTIANITE      .690     9.250  11.789    .000               147.6294
      2     1.000 800     1.000 140
8646002 TALC            35.005   -23.055 -18.988 -23.088               379.2888
      4    -4.000   2     3.000 460     4.000 770    -6.000 330
6050002 THENARDITE        .572      .179    .000    .000               142.0412
      2     2.000 500     1.000 732
5050001 THERMONATR       2.802     -.125    .000    .000               124.0043
      3     2.000 500     1.000 140     1.000   2
8215001 TREMOLITE       96.615   -56.546    .000    .000               812.4096
      5    -8.000   2     2.000 150     5.000 460     8.000 770 -14.000 330
7028001 VIVIANITE         .000    36.000    .000    .000               501.6062
      3     3.000 280     2.000 580     8.000   2
5010000 WITHERITE        -.360     8.585  13.335    .000               197.3494
      2     1.000 100     1.000 140
2047000 PYROLUSITE      29.180   -15.861    .000 -16.038                86.9368
      4    -4.000 330    -1.000   1     1.000 471     2.000   2
2047001 BIRNESSITE        .000   -18.091    .000    .000                86.9368
      4    -4.000 330    -1.000   1     1.000 471     2.000   2
2047002 NSUTITE           .000   -17.504    .000    .000                86.9368
      4    -4.000 330    -1.000   1     1.000 471     2.000   2
3047100 BIXBYITE        15.245      .611   2.226    .430               157.8742
      3    -6.000 330     2.000 471     3.000   2
3047000 HAUSMANNITE     80.140   -61.540    .000    .000               228.8116
      4    -8.000 330    -2.000   1     3.000 470     4.000   2
2047003 PYROCROITE      22.590   -15.088    .000 -15.381                88.9528
      3    -2.000 330     1.000 470     2.000   2
2047100 MANGANITE         .000      .238    .000    .000                87.9448
      3    -3.000 330     1.000 471     2.000   2
5047000 RHODOCHROSIT     2.079    10.410  11.019   9.993               114.9474
      2     1.000 470     1.000 140
4147000 MNCL2, 4H2O    -17.380    -2.710    .000    .000               197.9052
      3     1.000 470     2.000 180     4.000   2
1047000 MNS GREEN        5.790    -3.800    .000    .000                87.0020
      3    -1.000 330     1.000 470     1.000 730
6047000 MNSO4           15.480    -2.669    .000    .000               150.9996
      2     1.000 470     1.000 732
6047100 MN2(SO4)3       39.060     5.711    .000    .000               398.0608
      2     2.000 471     3.000 732
7047000 MN3(PO4)2       -2.120    23.827    .000    .000               354.7568
      2     3.000 470     2.000 580
0023000 CU METAL       -17.130     8.760    .000   8.800                63.5460
      2     1.000 230     1.000   1
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4123000 NANTOKITE     -9.980     6.760    .000   6.630                98.9990
      2     1.000 230     1.000 180
4223000 CUF           12.370    -7.080    .000    .000                82.5444
      2     1.000 230     1.000 270
2023000 CUPRITE       -6.245     1.550   1.870    .700               143.0914
      3    -2.000 330     2.000 230     1.000   2
1023000 CHALCOCITE   -49.350    34.619  34.920  30.900               159.1560
      3    -1.000 330     2.000 230     1.000 730
1023001 DJURLEITE    -47.881    33.920    .000    .000               154.9620
      4    -1.000 330      .066 231     1.868 230     1.000 730
1023002 ANILITE      -43.535    31.878    .000    .000               143.2695
      4    -1.000 330      .250 231     1.500 230     1.000 730
1023003 BLAUBLEI II     .000    27.279    .000    .000               121.0284
      4    -1.000 330      .600 231      .800 230     1.000 730
1023100 BLAUBLEI I      .000    24.162    .000    .000               101.9646
      4    -1.000 330      .900 231      .200 230     1.000 730
1023101 COVELLITE    -24.010    23.038    .000  22.170                95.6100
      3    -1.000 330     1.000 231     1.000 730
6023000 CU2SO4         4.560     1.950    .000    .000               223.1536
      2     2.000 230     1.000 732
3023000 CUPROUSFERIT   3.800     8.920    .000   6.880               151.3918
      4    -4.000 330     1.000 230     1.000 281     2.000   2
4123100 MELANOTHALLI  12.320    -3.730    .000  -4.450               134.4520
      2     1.000 231     2.000 180
5023100 CUCO3           .000     9.630   9.650   9.610               123.5552
      2     1.000 231     1.000 140
4223100 CUF2          13.320      .620    .000    .000               101.5428
      2     1.000 231     2.000 270
4223101 CUF2, 2H2O     3.650     4.550    .000    .000               137.5732
      3     1.000 231     2.000 270     2.000   2
2023100 CU(OH)2       15.250    -8.640    .000  -9.200                97.5606
      3    -2.000 330     1.000 231     2.000   2
4123101 ATACAMITE     18.690    -7.340  -7.240  -7.490               213.5669
      4    -3.000 330     2.000 231     3.000   2     1.000 180
5123100 CU2(OH)3NO3   17.350    -9.240    .000  -9.310               240.1188
      4    -3.000 330     2.000 231     3.000   2     1.000 492
6023100 ANTLERITE       .000    -8.290    .000  -8.900               354.7248
      4    -4.000 330     3.000 231     4.000   2     1.000 732
6023101 BROCHANTITE     .000   -15.340 -15.150 -15.500               452.2854
      4    -6.000 330     4.000 231     6.000   2     1.000 732
6023102 LANGITE       39.610   -16.790    .000 -17.400               470.3006
      4    -6.000 330     4.000 231     7.000   2     1.000 732
2023101 TENORITE      15.240    -7.620  -7.350  -7.890                79.5454
      3    -2.000 330     1.000 231     1.000   2
6023103 CUOCUSO4      35.575   -11.530    .000    .000               239.1490
      4    -2.000 330     2.000 231     1.000   2     1.000 732
7023100 CU3(PO4)2       .000    36.850    .000  36.900               380.5808
      2     3.000 231     2.000 580
7023101 CU3(PO4)2,3W    .000    35.120    .000    .000               434.6264
      3     3.000 231     2.000 580     3.000   2
6023104 CUSO4         18.140    -3.010  -2.630  -3.420               159.6036
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      2      1.000 231   1.000 732
6023105 CHALCANTHITE    -1.440     2.640   2.960   2.135               249.6796
      3      1.000 231   1.000 732      5.000   2
2023102 DIOPTASE         8.960    -6.500    .000    .000               157.6449
      3     -2.000 330   1.000 231      1.000 770
3023100 CUPRICFERIT     38.690    -5.880  -5.350    .000               239.2376
      4     -8.000 330   1.000 231      2.000 281     4.000   2
1023102 CHALCOPYRITE   -35.480    35.270    .000  30.790               183.5130
      4     -2.000 330   1.000 231      1.000 280     2.000 730
4023000 CUBR           -13.080     8.210    .000    .000               143.4500
      2      1.000 230   1.000 130
4323000 CUI            -20.140    11.890    .000    .000               190.4505
      2      1.000 230   1.000 380
0095000 ZN METAL        36.780   -25.757    .000 -25.790                65.3800
      2      1.000 950   2.000   1
4195000 ZNCL2           17.480    -7.030    .000  -7.060               136.2860
      2      1.000 950   2.000 180
5095000 SMITHSONITE      4.360    10.000  10.810   9.820               125.3892
      2      1.000 950   1.000 140
5095001 ZNCO3, 1H2O       .000    10.260    .000    .000               143.4044
      3      1.000 950   1.000 140      1.000   2
4295000 ZNF2            13.080     1.520    .000   1.080               103.3768
      2      1.000 950   2.000 270
2095000 ZN(OH)2 (A)       .000   -12.450 -12.260 -12.480                99.3946
      3     -2.000 330   1.000 950      2.000   2
2095001 ZN(OH)2 (C)       .000   -12.200    .000    .000                99.3946
      3     -2.000 330   1.000 950      2.000   2
2095002 ZN(OH)2 (B)       .000   -11.750 -11.320 -11.890                99.3946
      3     -2.000 330   1.000 950      2.000   2
2095003 ZN(OH)2 (G)       .000   -11.710 -11.190 -11.840                99.3946
      3     -2.000 330   1.000 950      2.000   2
2095004 ZN(OH)2 (E)       .000   -11.500 -10.950 -11.620                99.3946
      3     -2.000 330   1.000 950      2.000   2
4195001 ZN2(OH)3CL        .000   -15.200    .000    .000               217.2349
      4     -3.000 330   2.000 950      3.000   2     1.000 180
4195002 ZN5(OH)8CL2       .000   -38.500    .000    .000               533.8644
      4     -8.000 330   5.000 950      8.000   2     2.000 180
6095000 ZN2(OH)2SO4       .000    -7.500    .000    .000               260.8322
      4     -2.000 330   2.000 950      2.000   2     1.000 732
6095001 ZN4(OH)6SO4       .000   -28.400    .000    .000               459.6214
      4     -6.000 330   4.000 950      6.000   2     1.000 732
5195000 ZNNO3)2,6H2O    -5.510    -3.440    .000    .000               297.4810
      3      1.000 950   2.000 492      6.000   2
2095005 ZNO(ACTIVE)       .000   -11.310 -11.570 -11.860                81.3794
      3     -2.000 330   1.000 950      1.000   2
2095006 ZINCITE         21.860   -11.140 -10.990 -11.540                81.3794
      3     -2.000 330   1.000 950      1.000   2
6095002 ZN3O(SO4)2      62.000   -19.020    .000    .000               404.2546
      4     -2.000 330   3.000 950      2.000 732     1.000   2
7095000 ZN3(PO4),4W       .000    32.040    .000    .000               458.1436
      3      3.000 950   2.000 580      4.000   2
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1095000 ZNS (A)         -3.670      9.052    .000    .000                 97.4400
      3    -1.000 330    1.000 950      1.000 730
1095001 SPHALERITE      -8.250     11.618  13.212   5.952                 97.4400
      3    -1.000 330    1.000 950      1.000 730
1095002 WURTZITE        -5.060      9.682  10.182   8.552                 97.4400
      3    -1.000 330    1.000 950      1.000 730
8295000 ZNSIO3          18.270     -2.930    .000    .000                141.4637
      4    -2.000 330   -1.000   2      1.000 950     1.000 770
8095000 WILLEMITE       33.370    -15.330 -13.350    .000                220.8431
      3    -4.000 330    2.000 950      1.000 770
6095003 ZINCOSITE       19.200     -3.010    .000  -3.930                161.4376
      2     1.000 950    1.000 732
6095004 ZNSO4, 1H2O     10.640       .570    .000    .500                179.4528
      3     1.000 950    1.000 732      1.000   2
6095005 BIANCHITE         .160      1.765    .000   1.020                269.5288
      3     1.000 950    1.000 732      6.000   2
6095006 GOSLARITE       -3.300      1.960    .000   1.870                287.5440
      3     1.000 950    1.000 732      7.000   2
4095000 ZNBR2, 2H2O      7.510     -5.210    .000    .000                261.2184
      3     1.000 950    2.000 130      2.000   2
4395000 ZNI2            13.440     -7.230    .000    .000                319.1890
      2     1.000 950    2.000 380
0016000 CD METAL        18.000    -13.490    .000 -13.640                112.4100
      2     1.000 160    2.000   1
0016001 GAMMA CD        18.140    -13.590    .000    .000                112.4100
      2     1.000 160    2.000   1
5016000 OTAVITE           .580     13.740  13.810  11.210                172.4192
      2     1.000 160    1.000 140
4116000 CDCL2            4.470       .680    .000    .470                183.3160
      2     1.000 160    2.000 180
4116001 CDCL2, 1H2O      1.820      1.710    .000    .000                201.3312
      3     1.000 160    2.000 180      1.000   2
4116002 CDCL2,2.5H2O    -1.710      1.940    .000    .000                228.3536
      3     1.000 160    2.000 180      2.500   2
4216000 CDF2             9.720      2.980    .000    .000                150.4068
      2     1.000 160    2.000 270
2016000 CD(OH)2 (A)     20.770    -13.730 -13.610 -14.300                146.4246
      3    -2.000 330    1.000 160      2.000   2
2016001 CD(OH)2 (C)       .000    -13.650    .000    .000                146.4246
      3    -2.000 330    1.000 160      2.000   2
4116003 CDOHCL           7.407     -3.520  -3.300    .000                164.8703
      4    -1.000 330    1.000 160      1.000   2     1.000 180
6016000 CD3(OH)4SO4       .000    -22.560    .000    .000                501.3168
      4    -4.000 330    3.000 160      4.000   2     1.000 732
6016001 CD3OH2(SO4)2      .000     -6.710    .000    .000                563.3598
      4    -2.000 330    3.000 160      2.000   2     2.000 732
6016002 CD4(OH)6SO4       .000    -28.400    .000    .000                647.7414
      4    -6.000 330    4.000 160      6.000   2     1.000 732
2016002 MONTEPONITE     24.760    -15.120    .000 -15.740                128.4094
      3    -2.000 330    1.000 160      1.000   2
7016000 CD3(PO4)2         .000     32.600    .000    .000                527.1728
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      2     3.000 160    2.000 580
8216000 CDSI03          16.630    -9.060  -7.960    .000               188.4937
      4    -1.000   2    1.000 160       1.000 770     -2.000 330
6016003 CDS04           14.740      .100    .130    .050               208.4676
      2     1.000 160    1.000 732
6016004 CDS04, 1H20      7.520     1.657   1.680   1.630               226.4828
      3     1.000 160    1.000 732       1.000   2
6016005 CDS04,2.7H20     4.300     1.873   1.890   1.860               256.3879
      3     1.000 160    1.000 732       2.670   2
1016000 GREENOCKITE    -16.360    15.930    .000  13.112               144.4700
      3    -1.000 330    1.000 160       1.000 730
4016000 CDBR2, 4H20     -7.230     2.420    .000    .000               344.2788
      3     1.000 160    2.000 130       4.000   2
4316000 CDI2            -4.080     3.610    .000    .000               366.2190
      2     1.000 160    2.000 380
0060000 PB METAL         -.400    -4.270  -4.070  -4.310               207.2000
      2     1.000 600    2.000   1
4160000 COTUNNITE       -5.600     4.770   4.976   4.670               278.1060
      2     1.000 600    2.000 180
4160001 MATLOCKITE      -7.950     9.430    .000   8.600               261.6514
      3     1.000 600    1.000 180       1.000 270
4160002 PHOSGENITE        .000    19.810  19.940    .000               545.3152
      3     2.000 600    2.000 180       1.000 140
5060000 CERRUSITE       -4.860    13.130  13.440  12.830               267.2092
      2     1.000 600    1.000 140
4260000 PBF2              .700     7.440   7.570    .000               245.1968
      2     1.000 600    2.000 270
2060000 MASSICOT        16.780   -12.910 -12.790    .000               223.1994
      3    -2.000 330    1.000 600       1.000   2
2060001 LITHARGE        16.380   -12.720 -12.640 -13.070               223.1994
      3    -2.000 330    1.000 600       1.000   2
2060002 PBO, .3H20        .000   -12.980    .000    .000               229.1444
      3    -2.000 330    1.000 600       1.330   2
5060001 PB20C03         11.460      .500    .780    .000               490.4086
      4    -2.000 330    2.000 600       1.000   2     1.000 140
6060000 LARNAKITE        6.440      .280   6.300    .000               526.4570
      4    -2.000 330    2.000 600       1.000 732     1.000   2
6060001 PB302S04        20.750   -10.400    .000    .000               749.6564
      4    -4.000 330    3.000 600       1.000 732     2.000   2
6060002 PB403S04        35.070   -22.100    .000    .000               972.8558
      4    -6.000 330    4.000 600       1.000 732     3.000   2
7060001 CLPYROMORPH       .000    84.430    .000  34.510              1356.3672
      3     5.000 600    3.000 580       1.000 180
7060002 HXYPYROMORPH      .000    62.790    .000    .000              1337.9215
      4    -1.000 330    5.000 600       3.000 580     1.000   2
5060002 PB302C03        26.430   -11.020    .000    .000               713.6080
      4    -4.000 330    3.000 600       1.000 140     2.000   2
7060003 PLUMBGUMMITE      .000    32.790    .000    .000               581.1391
      5    -5.000 330    1.000 600       3.000  30     2.000 580     6.000   2
7060004 HINSDALITE        .000     2.500    .000    .000               581.2174
      6    -6.000 330    1.000 600       3.000  30     1.000 580     1.000 732     6.00 002
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7060005 TSUMEBITE          .000     9.790    .000    .000               677.9849
     .5    -3.000 330     2.000 600     1.000 231     1.000 580     6.000   2
8260000 PBSIO3            9.260    -7.320  -6.120  -7.640               283.2837
      4    -1.000   2    -2.000 330     1.000 600     1.000 770
8060000 PB2SIO4          26.000   -19.760 -19.220 -20.050               506.4831
      3    -4.000 330     2.000 600     1.000 770
6060003 ANGLESITE        -2.150     7.790   7.870    .000               303.2576
      2     1.000 600     1.000 732
1060001 GALENA          -19.400    15.132  16.452  13.682               239.2600
      3    -1.000 330     1.000 600     1.000 730
2060003 PLATTNERITE      70.730   -49.300 -49.000    .000               239.1988
      4    -4.000 330    -2.000   1     1.000 600     2.000   2
3060000 PB2O3              .000   -61.040    .000    .000               462.3982
      4    -6.000 330    -2.000   1     2.000 600     3.000   2
3060001 MINIUM          102.760   -73.690 -70.800    .000               685.5976
      4    -8.000 330    -2.000   1     3.000 600     4.000   2
2060004 PB(OH)2 (C)      13.990    -8.150    .000 -13.630               241.2146
      3    -2.000 330     1.000 600     2.000   2
4160003 LAURIONITE         .000     -.623   -.175    .000               259.6603
      4    -1.000 330     1.000 600     1.000 180     1.000   2
4160004 PB2(OH)3CL         .000    -8.793    .000    .000               500.8749
      4    -3.000 330     2.000 600     3.000   2     1.000 180
5060003 HYDCERRUSITE       .000    17.460    .000    .000               775.6330
      4    -2.000 330     3.000 600     2.000 140     2.000   2
2060005 PB2O(OH)2          .000   -26.200    .000 -27.100               464.4140
      3    -4.000 330     2.000 600     3.000   2
4060000 PBBR2            -8.100     5.180   5.340   4.410               367.0080
      2     1.000 600     2.000 130
4060001 PBBRF              .000     8.490    .000    .000               306.1024
      3     1.000 600     1.000 130     1.000 270
4360000 PBI2            -15.160     8.070    .000    .000               461.0090
      2     1.000 600     2.000 380
6060004 PB4(OH)6SO4        .000   -21.100    .000    .000              1026.9014
      4    -6.000 330     4.000 600     1.000 732     6.000   2
5054000 NICO3             9.940     6.840    .000    .000               118.7092
      2     1.000 540     1.000 140
2054000 NI(OH)2         -30.450   -10.800 -10.590 -13.300                92.7146
      3    -2.000 330     1.000 540     2.000   2
6054000 NI4(OH)6SO4        .000   -32.000    .000    .000               432.9014
      4    -6.000 330     4.000 540     1.000 732     6.000   2
2054001 BUNSENITE        23.920   -12.450    .000 -12.390                74.6994
      3    -2.000 330     1.000 540     1.000   2
7054000 NI3(PO4)2          .000    31.300    .000    .000               366.0428
      2     3.000 540     2.000 580
1054000 MILLERITE        -2.500     8.042   8.132    .000                90.7600
      3    -1.000 330     1.000 540     1.000 730
6054001 RETGERSITE       -1.100     2.040    .000    .000               262.8488
      3     1.000 540     1.000 732     6.000   2
6054002 MORENOSITE       -2.940     2.360    .000    .000               280.8640
      3     1.000 540     1.000 732     7.000   2
8054000 NI2SIO4          33.360   -14.540    .000    .000               209.4831
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      3   -4.000 330    2.000 540    1.000 770
0002000 AG METAL     -25.234  13.510    .000    .000            107.8680
      2    1.000  20    1.000   1
4002000 BROMYRITE    -20.170  12.270    .000    .000            187.7720
      2    1.000  20    1.000 130
4102000 CERARGYRITE  -15.652   9.750    .000    .000            143.3210
      2    1.000  20    1.000 180
5002000 AG2CO3        -9.530  11.070    .000    .000            275.7452
      2    2.000  20    1.000 140
4202000 AGF.4H2O      -4.270   -.550    .000    .000            198.9272
      3    1.000  20    1.000 270    4.000   2
4302000 IODYRITE     -26.820  16.070    .000    .000            234.7725
      2    1.000  20    1.000 380
2002000 AG2O          10.430 -12.580    .000    .000            231.7354
      3   -2.000 330    2.000  20    1.000   2
7002000 AG3PO4          .000  17.550    .000    .000            418.5754
      2    3.000  20    1.000 580
1002000 ACANTHITE    -53.300  36.050    .000    .000            247.7960
      3   -1.000 330    2.000  20    1.000 730
6002000 AG2SO4        -4.250   4.920    .000    .000            311.7936
      2    2.000  20    1.000 732
8450001 ANALCIME      22.840  -6.719    .000    .000            220.1550
      5    1.000 500    1.000  30    2.000 770   -1.000   2   -4.000 330
8603000 HALLOYSITE    39.730  -8.994    .000    .000            258.1620
      4    2.000  30    2.000 770    1.000   2   -6.000 330
8603001 KAOLINITE     35.280  -5.726    .000    .000            258.1620
      4    2.000  30    2.000 770    1.000   2   -6.000 330
8415000 LEONHARDITE   85.360 -16.490    .000    .000            922.8670
      5   -1.000   2  -16.000 330    2.000 150    8.000 770    4.000  30
8450002 LOW ALBITE    17.400  -2.592    .000    .000            262.2250
      5    1.000 500    1.000  30    3.000 770   -4.000 330   -4.000   2
8450003 ANALBITE      20.000  -3.506    .000    .000            262.2250
      5    1.000 500    1.000  30    3.000 770   -4.000 330   -4.000   2
8641000 MUSCOVITE     59.340 -12.990    .000    .000            398.3110
      4    1.000 410    3.000  30    3.000 770  -10.000 330
8641001 ANNITE        65.720 -23.290    .000    .000            511.8900
      5    1.000 410    3.000 280    1.000  30    3.000 770  -10.000 330
8415001 ANORTHITE     70.660 -25.430    .000    .000            278.2110
      4    1.000 150    2.000  30    2.000 770   -8.000 330
8603002 PYROPHYLLITE    .000   1.598    .000    .000            360.3138
      4    2.000  30    4.000 770   -4.000   2   -6.000 330
8415002 LAUMONTITE    50.450 -14.460    .000    .000            470.4410
      4    1.000 150    2.000  30    4.000 770   -8.000 330
8415003 WAIRAKITE     63.150 -18.870    .000    .000            434.4110
      5    1.000 150    2.000  30    4.000 770   -8.000 330   -2.000   2
5023101 MALACHITE     15.610   5.180    .000   3.940            221.1162
      4    2.000 231    2.000   2    1.000 140   -2.000 330
5023102 AZURITE       23.770  16.920    .000    .000            344.6716
      4    3.000 231    2.000   2    2.000 140   -2.000 330
3006000 ARSENOLITE   -14.330   2.801   2.859   2.728            395.6824
      2    4.000  60   -6.000   2
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3006001 CLAUDETITE       -13.290     3.065    .000   3.021               395.6824
      2      4.000  60    -6.000  2
4306000 ASI3              -1.875    -4.155    .000    .000               455.6347
      4      1.000  60     3.000 380     3.000 330   -3.000   2
1006000 ORIPMENT         -82.890    60.971    .000  46.004               246.0350
      4      2.000  60     3.000 730     3.000 330   -6.000   2
1006001 REALGAR          -30.545    19.747  26.574    .000               106.9855
      5      1.000  60     1.000 730     2.000 330    1.000   1   -3.000   2
3006100 AS205              5.405    -6.699    .000  -9.478               229.8400
      2      2.000  61    -3.000  2
5295000 ZN(BO2)2            .000    -8.290    .000    .000               150.9893
      4     -2.000   2    -2.000 330     1.000 950    2.000  90
5216000 CD(BO2)2            .000    -9.840    .000    .000               198.0188
      4     -2.000   2    -2.000 330     1.000 160    2.000  90
5260000 PB(BO2)2           5.800    -7.610    .000    .000               292.8093
      4     -2.000   2    -2.000 330     1.000 600    2.000  90
7047001 MNHPO4(C)           .000    25.400    .000    .000               150.9174
      3      1.000 470     1.000 580     1.000 330
7060006 PBHPO4              .000    23.900    .000    .000               303.1693
      3      1.000 600     1.000 580     1.000 330
7060007 PB3(PO4)2           .000    44.500    .000    .000               811.5125
      2      3.000 600     2.000 580
0073100 SULFUR             4.200     2.110    .000    .000                32.0640
      3      1.000 730    -1.000 330    -2.000   1
7203000 ALASO4.2W           .000    -4.800    .000    .000               165.9006
      4      1.000  30     1.000  61     2.000   2   -3.000 330
7215000 CA3(ASO4)26W        .000   -22.300    .000    .000               506.1700
      4      3.000 150     2.000  61     4.000   2   -6.000 330
7223100 CU3(ASO4)26W        .000    -6.100    .000    .000               576.5680
      4      3.000 231     2.000  61     2.000   2   -6.000 330
7228100 FEASO4.2W           .000     -.400    .000    .000               230.7967
      4      1.000 281     1.000  61     2.000   2   -3.000 330
7247000 MN3ASO428W          .000   -12.500    .000    .000               586.7746
      4      3.000 470     2.000  61     8.000   2   -6.000 330
7254000 NI3(ASO4)28W        .000   -15.700    .000    .000               459.1707
      4      3.000 540     2.000  61     8.000   2   -6.000 330
7260000 PB3(ASO4)2          .000    -5.800    .000    .000               899.4079
      3      3.000 600     2.000  61    -6.000 330
7295000 ZN3ASO422.5W        .000   -13.650    .000    .000               518.9862
      4      3.000 950     2.000  61     2.500   2   -6.000 330
7210000 BA(ASO4)2         -2.640     8.910    .000    .000               689.8582
      3      3.000 100     2.000  61    -6.000 330
0090000 V METAL           62.900   -42.350    .000    .000                50.9400
      2      1.000 901     3.000   1
2090000 VO                28.020   -13.080    .000    .000                66.9390
      4     -2.000 330     1.000 901     1.000   2    1.000   1
4190000 VCL2              35.800   -17.970    .000    .000               121.8460
      3      1.000 901     2.000 180     1.000   1
3090100 V203              39.445    -9.800    .000    .000               149.8780
      3     -6.000 330     2.000 901     3.000   2
2090100 V(OH)3              .000    -7.650    .000    .000               101.9620
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       3    -3.000 330        1.000 901      3.000   2
4190100 VCL3                 43.960    -21.730     .000      .000                  157.2990
       2     1.000 901        3.000 180
4190101 VOCL                 26.170     -9.410     .000      .000                  137.8450
       4     1.000 901        1.000 180      1.000   2     -2.000 330
3090200 V204                 28.130     -8.547     .000      .000                  165.8780
       3    -4.000 330        2.000 902      2.000   2
2090200 VO(OH)2                .000     -5.850     .000      .000                  100.9540
       3    -2.000 330        1.000 902      2.000   2
4290200 VF4                  47.590    -14.930     .000      .000                  126.9320
       4    -1.000   2        1.000 902      4.000 270      2.000 330
6090200 VOS04 (C)            20.720     -3.570     .000      .000                  162.9970
       2     1.000 902        1.000 732
7090200 (VO)3(P04)2            .000     25.097     .000      .000                  390.7530
       2     3.000 902        2.000 580
4190200 VOCL2                28.200    -12.790     .000      .000                  137.8450
       2     1.000 902        2.000 180
3090300 V205                  8.315      1.437     .000      .000                  181.8770
       3    -2.000 330        2.000 903      1.000   2
7315000 TYUYAMUNITE          36.600     -4.075     .000      .000                  810.0130
       5    -8.000 330        1.000 150      2.000 893      2.000 903      4.000   2
7315001 CA-VANADATE          20.260     -5.665     .000      .000                  237.9560
       4    -4.000 330        1.000 150      2.000 903      2.000   2
7315002 CA3(V04)2            70.130    -38.963     .000      .000                  350.1150
       4    -8.000 330        3.000 150      2.000 903      4.000   2
7315003 CA2V207              38.125    -17.495     .000      .000                  294.0360
       4    -6.000 330        2.000 150      2.000 903      3.000   2
7328000 FE-VANADATE          14.730      3.716     .000      .000                  508.4310
       4    -4.000 330        1.000 280      2.000 903      2.000   2
7346000 MG-VANADATE          32.660    -11.259     .000      .000                  222.1860
       4    -4.000 330        1.000 460      2.000 903      2.000   2
7346001 MG2V207              61.005    -26.366     .000      .000                  262.4960
       4    -6.000 330        2.000 460      2.000 903      3.000   2
7347000 MN-VANADATE          22.090     -4.896     .000      .000                  252.8160
       4    -4.000 330        1.000 470      2.000 903      2.000   2
7349000 NH4V03                3.770     -2.690     .000      .000                  116.9770
       4    -2.000 330        1.000 490      1.000 903      1.000   2
7350000 NA-VANADATE           7.010     -3.710     .000      .000                  121.9280
       4    -2.000 330        1.000 500      1.000 903      1.000   2
7350001 NA3V04               44.420    -36.940     .000      .000                  183.9080
       4    -4.000 330        3.000 500      1.000 903      2.000   2
7350002 NA4V207              48.065    -37.404     .000      .000                  305.8360
       4    -6.000 330        4.000 500      2.000 903      3.000   2
7360000 PB3(V04)2            17.360     -6.120     .000      .000                  851.4750
       4    -8.000 330        3.000 600      2.000 903      4.000   2
7360001 PB2V207               6.445      1.884     .000      .000                  628.2760
       4    -6.000 330        2.000 600      2.000 903      3.000   2
7346002 CARNOTITE            17.400      -.498     .000      .000                  848.1330
       5    -8.000 330        2.000 410      2.000 893      2.000 903      4.000   2
7302000 AG-VANADATE            .000      -.770     .000      .000                  206.8080
       4    -2.000 330        1.000  20      1.000 903      1.000   2
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7302001 AG2HVO4           .000    -1.480    .000    .000              331.6860
      4   -3.000 330     2.000 20      1.000 903     2.000   2
7302002 AG3H2VO5          .000    -5.180    .000    .000              456.5630
      4   -4.000 330     3.000 20      1.000 903     3.000   2
4190300 VO2CL            9.650    -2.810    .000    .000              118.3920
      2    1.000 903     1.000 180
3090101 V3O5            23.530    -1.870    .000    .000              232.8170
      4   -4.000 330     3.000 902     2.000   2     2.000   1
3090201 V4O7            39.150    -7.140    .000    .000              315.7560
      4   -6.000 330     4.000 902     3.000   2     2.000   1
3090202 V6O13          -64.890    60.860    .000    .000              513.6320
      4   -2.000 330     6.000 903     1.000   2     4.000   1
2015000 LIME            46.265   -32.797       0       0                     0
      3   -2.000 330     1.000 150     1.000 002
2015001 PORTLANDITE     30.690   -22.675       0       0                     0
      3   -2.000 330     1.000 150     2.000 002
2028000 WUSTITE         24.846   -11.687       0       0                     0
      3   -2.000 330     0.947 280     1.000 002
2046001 PERICLASE       36.135   -21.510       0       0                     0
      3   -2.000 330     1.000 460     1.000 002
3028001 HERCYNITE       78.360   -27.162       0       0                     0
      4   -8.000 330     1.000 280     2.000 030     4.000 002
3046000 SPINEL          89.089   -36.333       0       0                     0
      4   -8.000 330     1.000 460     2.000 030     4.000 002
3046001 MAG-FERRITE     66.639   -16.765       0       0                     0
      4   -8.000 330     1.000 460     2.000 281     4.000 002
4250000 CRYOLITE       -10.904    31.490       0       0                     0
      3    1.000 030     3.000 500     6.000 270
8215002 WOLLASTONITE    19.498   -12.996       0       0                     0
      4   -1.000 002    -2.000 330     1.000 770     1.000 150
8215003 P-WOLLSTANIT    21.068   -13.846       0       0                     0
      4   -1.000 002    -2.000 330     1.000 770     1.000 150
8015001 CA-OLIVINE      54.695   -37.649       0       0                     0
      3   -4.000 330     1.000 770     2.000 150
8015002 LARNITE         57.238   -39.141       0       0                     0
      3   -4.000 330     1.000 770     2.000 150
8015007 CA3SIO5        106.335   -73.867       0       0                     0
      4   -6.000 330     1.000 770     3.000 150     1.000 002
8015003 MONTICELLITE    49.421   -30.272       0       0                     0
      4   -4.000 330     1.000 770     1.000 150     1.000 460
8015005 AKERMINITE      76.445   -47.472       0       0                     0
      5   -1.000 002    -6.000 330     2.000 770     2.000 150     1.000 460
8015004 MERWINITE      107.111   -68.543       0       0                     0
      4   -8.000 330     2.000 770     1.000 460     3.000 150
8441000 KALSILITE       28.919   -12.838       0       0                     0
      4   -4.000 330     1.000 770     1.000 030     1.000 410
8441001 LEUCITE         22.085    -6.423       0       0                     0
      5   -2.000 002    -4.000 330     2.000 770     1.000 030     1.000 410
8441002 MICROCLINE      12.309    -0.616       0       0                     0
      5   -4.000 002    -4.000 330     3.000 770     1.000 030     1.000 410
8441003 H SANIDINE      14.252    -1.062       0       0                     0
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      5    -4.000 002    -4.000 330     3.000 770     1.000 030     1.000 410
8450004 NEPHELINE       33.204    -14.218      0       0                      0
      4    -4.000 330     1.000 770     1.000 030     1.000 500
8015006 GEHLENITE      116.125   -56.822       0       0                      0
      5   -10.000 330     2.000 030     1.000 770     2.000 150     3.000 002
2028103 LEPIDOCROCIT         0    -1.371       0       0                      0
      3    -3.000 330     1.000 281     2.000 002
8650000 NA-NONTRONIT         0    14.504  12.122  16.886                      0
      6    -7.320 330    -2.680 002     0.330 030     2.000 281     0.330 500    3.670 770
8641002 K-NONTRONITE         0    15.549  12.763  18.334                      0
      6    -7.320 330    -2.680 002     0.330 030     2.000 281     0.330 410    3.670 770
8615000 CA-NONTRONIT         0    20.889  19.057  22.722                      0
      6    -7.320 330    -2.680 002     0.330 030     2.000 281     0.167 150    3.670 770
8646005 MG-NONTRONIT         0    20.589  19.013  22.165                      0
      6    -7.320 330    -2.680 002     0.330 030     2.000 281     0.167 460    3.670 770
0048000 MO (C)         -34.760    19.690                               95.940
      4    -4.000 002     1.000 480     8.000 330     6.000 001
2048001 MO02 (C)       -38.630    29.970                               127.94
      4    -2.000 002     1.000 480     4.000 330     2.000 001
2048002 MOLYBDITE      -7.915     12.070                               143.94
      3    -1.000 002     1.000 480     2.000 330
2048003 H2MO04 (C)     -11.500    13.330                               161.95
      2     1.000 480     2.000 330
1048000 MOLYBDENITE    -92.16     70.590                               160.16
      5    -4.000 002     1.000 480     2.000 730     6.000 330     2.000 001
7402000 AG2MO04        -12.950    11.550                               375.67
      2     1.000 480     2.000 020
7410000 BAMO04         -0.350       8.26                               297.27
      2     1.000 480     1.000 100
7415000 POWELLITE      -0.160      7.840                               200.02
      2     1.000 480     1.000 150
7423100 CUMO04         -1.980      6.480                               223.48
      2     1.000 480     1.000 231
7428000 FEMO04          2.800     10.450                               215.78
      2     1.000 480     1.000 280
7441000 K2MO04          0.880     -3.510                               238.13
      2     1.000 480     2.000 410
7446000 MGMO04         15.240      0.830                               184.24
      2     1.000 480     1.000 460
7447000 MNMO04         6.510       4.550                               214.88
      2     1.000 480     1.000 470
7450000 NA2MO04        2.310      -0.890                               205.92
      2     1.000 480     2.000 500
7450001 NA2MO207       -13.225     20.15                               349.86
      4    -1.000 002     2.000 480     2.000 500     2.000 330
7460000 WULFENITE      -12.500    15.830                               367.14
      2     1.000 480     1.000 600
7480000 SRMO04         -3.650       7.89                               247.56
      2     1.000 480     1.000 800
7495000 ZNMO04         8.680       4.490                               225.32
      2     1.000 480     1.000 950
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4148000 MOCL6          79.820    -49.800                               308.66
      4    -4.000 002     1.000 480     8.000 330     6.000 180
4148001 MOCL5          38.890    -21.110                               273.21
      5    -4.000 002     1.000 480     8.000 330     5.000 180     1.000 001
4148002 MOCL4          10.960     -1.850                               237.75
      5    -4.000 002     1.000 480     8.000 330     4.000 180     2.000 001
2048004 ILSEMANNITE               63.82                                415.82
      4     3.000 480     8.000 330     2.000 001    -4.000 002
7428001 FERRIMOLYBDT              35.96                                853.71
      4     3.520 480     9.880 002     1.040 330                   2.000 281
0085000 TH (C)   -123.510
      2     1.000 850     4.000 001
2085000 THO2 (C)                  -1.860
      3    -4.000 330     1.000 850     2.000 002
0185000 THH2 (C)                -105.990
      3     1.000 850     2.000 330     6.000 001
0185001 THH3.75                                                       -99.320
      3     1.000 850     3.750 330     7.750 001
4285000 THF4                      28.920
      2     1.000 850     4.000 270
4285001 THF4.2.5H2O               31.980
      3     1.000 850     4.000 270     2.500 002
4285002 THOF2                     14.690
      4    -2.000 330     1.000 850     2.000 270     1.000 002
4185000 THCL4                    -23.760
      2     1.000 850     4.000 180
4185003 THOCL2                    -8.540
      4    -2.000 330     1.000 850     2.000 180     1.000 002
1085000 THS                      -52.950
      4     1.000 850     1.000 730    -1.000 330     2.000 001
1085001 TH2S3                    -52.02
      4     2.000 850     3.000 730    -3.000 330     2.000 001
1085002 TH7S12                   -117.26
      4     7.000 850    12.000 730    -12.00 330     4.000 001
1085003 THS2                      -10.66
      3     1.000 850     2.000 730    -2.000 330
6085000 TH(SO4)2                  20.350
      2     1.000 850     2.000 732
5185000 TH(NO3)4.5W               -1.910
      3     1.000 850     4.000 492     5.000 002
0067000 RA (C)                   -98.370
      2     1.000 670     2.000 001
2067000 RAO (C)                  -53.800
      3    -2.000 330     1.000 670     1.000 002
4167000 RACL2.2H2O                 0.780
      3     1.000 670     2.000 002     2.000 180
6067000 RASO4 (C)                 10.430
      2     1.000 670     1.000 732
5167000 RA(NO3)2                   2.110
      2     1.000 670     2.000 492
5015007 MG-CALCITE                 8.14
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      3     0.920 150     0.080 460     1.000 140
6003008 JURBANITE                  3.80
      4     1.000  30     6.000   2     1.000 732    -1.000 330
6003009 BASALUMINITE             -23.98
      4     4.000  30     1.000 732    15.000   2   -10.000 330
2028106 FE(OH)3 SOIL              -2.70
      3     1.000 281     3.000   2    -3.000 330
0087000 Tl metal     -1.2800   -5.6733                0.00 0.00 0.00   204.3700
      2     1.000 870     1.000   1
2087000 Tl2O         23.0550  -27.0984                0.00 0.00 0.00   424.7394
      3     2.000 870     1.000   2    -2.000 330
2087001 TlOH          9.9350  -12.9225                0.00 0.00 0.00   221.3773
      3     1.000 870     1.000   2    -1.000 330
4187000 TlCl        -10.1370    3.7243                0.00 0.00 0.00   239.8230
      2     1.000 870     1.000 180
4087000 TlBr        -13.6410    5.4190                0.00 0.00 0.00   284.2740
      2     1.000 870     1.000 130
4387000 TlI         -17.2810    7.1964                0.00 0.00 0.00   331.2745
      2     1.000 870     1.000 380
1087000 Tl2S        -21.5600    7.1832                0.00 0.00 0.00   440.8000
      3     2.000 870     1.000 730    -1.000 330
6087000 Tl2SO4       -7.9400    3.6942                0.00 0.00 0.00   504.7976
      2     2.000 870     1.000 732
1187000 Tl2Se       -20.3600    6.6848                0.00 0.00 0.00   487.7000
      3     2.000 870     1.000 760    -1.000 330
6187000 Tl2SeO4      -9.7600    4.0168                0.00 0.00 0.00   551.6976
      2     2.000 870     1.000 762
5187000 TlNO3       -10.0200    1.5319                0.00 0.00 0.00   266.3749
      2     1.000 870     1.000 492
5087000 Tl2CO3       -8.0200    3.8482                0.00 0.00 0.00   468.7492
      2     2.000 870     1.000 140
2087101 Tl(OH)3       0.0000    6.4503                0.00 0.00 0.00   255.3919
      1     1.000 871
2087100 Avicennite    0.0000   16.3236                0.00 0.00 0.00   456.7382
      2     2.000 871    -3.000   2
  76000 Se hex,blac  -3.8000    7.6963                0.00 0.00 0.00   78.9600
      3     1.000 760    -1.000 330    -2.000   1
  76001 Se (A)       -2.6000    7.1099                0.00 0.00 0.00   78.9600
      3     1.000 760    -1.000 330    -2.000   1
1228001 Ferroselite -11.3000   18.5959                0.00 0.00 0.00   213.7670
      4     2.000 760     1.000 280    -2.000 330    -2.000   1
1260000 Clausthalit -28.0000   21.2162                0.00 0.00 0.00   286.1600
      3     1.000 760     1.000 600    -1.000 330
1202000 Ag2Se       -64.9500   43.6448                0.00 0.00 0.00   294.6960
      3     1.000 760     2.000  20    -1.000 330
1216000 CdSe        -18.1600   18.0739                0.00 0.00 0.00   191.3700
      3     1.000 760     1.000 160    -1.000 330
1223100 CuSe        -28.9500   26.5121                0.00 0.00 0.00   142.5060
      3     1.000 760     1.000 231    -1.000 330
1223000 Cu2Se alpha -51.2100   36.0922                0.00 0.00 0.00   206.0520
      3     1.000 760     2.000 230    -1.000 330
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1223101 CuSe2         -33.6000   33.3655                 0.00 0.00 0.00    221.4660
      4     2.000 760      1.000 231   -2.000  330    -2.000   1
1223001 Cu3Se2        -81.3400   63.4911                 0.00 0.00 0.00    348.5580
      4     2.000 760      2.000 230    1.000  231    -2.000 330
1228000 FeSe           -0.5000    7.1466                 0.00 0.00 0.00    134.8070
      3     1.000 760      1.000 280   -1.000  330
1247000 MnSe           13.4600   -5.3508                 0.00 0.00 0.00    133.8980
      3     1.000 760      1.000 470   -1.000  330
1295000 ZnSe           -6.4390   11.3642                 0.00 0.00 0.00    144.3400
      3     1.000 760      1.000 950   -1.000  330
1220000 CoSe            0.0000   16.2723                 0.00 0.00 0.00    137.8932
      3     1.000 760      1.000 200   -1.000  330
1254000 NiSe            0.0000   17.7382                 0.00 0.00 0.00    137.6600
      3     1.000 760      1.000 540   -1.000  330
2076100 Se02           -0.3350   -0.1246                 0.00 0.00 0.00    110.9588
      3     1.000 761      1.000 330   -1.000    2
6110000 BaSe03          6.2800   -4.1634                 0.00 0.00 0.00    264.2882
      3     1.000 761      1.000 100   -1.000  330
6115000 CaSe03:2H20     4.6500   -2.8139                 0.00 0.00 0.00    203.0686
      4     1.000 761      1.000 150    2.000    2    -1.000 330
6123100 CuSe03:2H20     8.8100   -0.4838                 0.00 0.00 0.00    226.5346
      4     1.000 761      1.000 231    2.000    2    -1.000 330
6128100 Fe2(Se03)3:     0.0000   20.6262                 0.00 0.00 0.00    528.5990
      4     3.000 761      2.000 281    2.000    2    -3.000 330
6128101 Fe2(OH)4Se0     0.0000   -1.5539                 0.00 0.00 0.00    306.6814
      4     1.000 761      2.000 281    4.000    2    -5.000 330
6146000 MgSe03:6H20    -1.2500   -4.0314                 0.00 0.00 0.00    259.3544
      4     1.000 761      1.000 460    6.000    2    -1.000 330
6147001 MnSE03:2H20    -2.0300   -0.9822                 0.00 0.00 0.00    217.9266
      4     1.000 761      1.000 470    2.000    2    -1.000 330
6154000 NiSe03:2H20     7.4100   -2.8147                 0.00 0.00 0.00    221.6886
      4     1.000 761      1.000 540    2.000    2    -1.000 330
6180000 SrSe03          0.0000   -0.1034                 0.00 0.00 0.00    214.5782
      3     1.000 761      1.000 800   -1.000  330
6147000 MnSe03          0.0000   -0.0440                 0.00 0.00 0.00    181.8962
      3     1.000 761      1.000 470   -1.000  330
6120000 CoSe03          0.0000   -0.1906                 0.00 0.00 0.00    185.8914
      3     1.000 761      1.000 200   -1.000  330
6102000 Ag2Se03        -9.4700    8.1977                 0.00 0.00 0.00    342.6942
      3     1.000 761      2.000 20    -1.000  330
2076200 Se03           34.9850  -21.0440                 0.00 0.00 0.00    126.9582
      3     1.000 762      2.000 330   -1.000    2
6102001 Ag2Se04       -10.4500    8.9014                 0.00 0.00 0.00    358.6936
      2     1.000 762      2.000 20
6110001 BaSe04         -2.0000    5.1895                 0.00 0.00 0.00    280.2876
      2     1.000 762      1.000 100
6115001 CaSe04:2H20    -0.8800    2.9473                 0.00 0.00 0.00    219.0680
      3     1.000 762      1.000 150    2.000    2
6160000 PbSe04         -3.8000    6.8387                 0.00 0.00 0.00    350.1576
      2     1.000 762      1.000 600
6180001 SrSe04         -2.6900    6.8747                 0.00 0.00 0.00    230.5776
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      2     1.000 762     1.000 800
  36000 Hg metal (1  -19.9350   13.4552                          0.00 0.00 0.00   200.5900
      2     0.500 360     1.000   1
4036000 Hg2Br2       -31.2520   22.2091                          0.00 0.00 0.00   560.9880
      2     1.000 360     2.000 130
5036000 Hg2CO3         0.0000   13.9586                          0.00 0.00 0.00   461.1892
      2     1.000 360     1.000 140
4136000 Calomel      -23.4440   17.8427                          0.00 0.00 0.00   472.0860
      2     1.000 360     2.000 180
4236000 Hg2F2          4.4320    3.0811                          0.00 0.00 0.00   439.1768
      2     1.000 360     2.000 270
4336000 Hg2I2          0.0000   28.2782                          0.00 0.00 0.00   654.9890
      2     1.000 360     2.000 380
2036000 Hg2(OH)2       0.0000   -5.2603                          0.00 0.00 0.00   435.1946
      3     1.000 360     2.000   2     -2.000 330
7036000 Hg2HPO4        0.0000   25.9795                          0.00 0.00 0.00   497.1593
      3     1.000 360     1.000 330     1.000 580
6036000 Hg2SO4        -0.2300    6.1593                          0.00 0.00 0.00   497.2376
      2     1.000 360     1.000 732
6136000 Hg2SeO3        0.0000    6.9290                          0.00 0.00 0.00   528.1382
      3     1.000 360     1.000 761    -1.000 330
4036100 HgBr2        -34.4520   25.3730                          0.00 0.00 0.00   360.3980
      4     1.000 361     2.000 130     2.000 330    -2.000   2
5036100 HgCO3        -22.1300   28.6817                          0.00 0.00 0.00   260.5992
      4     1.000 361     1.000 140     2.000 330    -2.000   2
4136100 HgCl2        -27.2640   21.7858                          0.00 0.00 0.00   271.4960
      4     1.000 361     2.000 180     2.000 330    -2.000   2
4336100 Coccinite    -49.7320   34.6599                          0.00 0.00 0.00   454.3990
      4     1.000 361     2.000 380     2.000 330    -2.000   2
2036100 Montroydite   -5.1150    3.6503                          0.00 0.00 0.00   216.5894
      2     1.000 361    -1.000   2
2036101 Hg(OH)2        0.0000    3.4963                          0.00 0.00 0.00   234.6046
      1     1.000 361
1036100 Cinnabar     -60.4300   45.1885                          0.00 0.00 0.00   232.6500
      4     1.000 361     1.000 730     1.000 330    -2.000   2
1036101 Metacinnaba  -59.5300   44.8220                          0.00 0.00 0.00   232.6500
      4     1.000 361     1.000 730     1.000 330    -2.000   2
6036100 HgSO4         -3.5100    9.4189                          0.00 0.00 0.00   296.6476
      4     1.000 361     1.000 732     2.000 330    -2.000   2
6136100 HgSeO3         0.0000   12.6953                          0.00 0.00 0.00   327.5482
      4     1.000 361     1.000 761     1.000 330    -2.000   2
4336102 HgI2:2NH3    -32.6320   16.1066                          0.00 0.00 0.00   488.4598
      4     1.000 361     2.000 380     2.000 490    -2.000   2
4336103 HgI2:6NH3     20.5680  -33.8566                          0.00 0.00 0.00   556.5814
      5     1.000 361     2.000 380     6.000 490    -2.000   2    -4.000 330
2021100 Cr(OH)2        8.5100  -10.8189                          0.00 0.00 0.00    86.0106
      3     1.000 210     2.000   2     -2.000 330
4021100 CrBR3         33.7770  -19.9086                          0.00 0.00 0.00   291.7080
      4     1.000 211     3.000 130     2.000 330    -2.000   2
4121100 CrCL3         27.5090  -13.5067                          0.00 0.00 0.00   158.3550
      4     1.000 211     3.000 180     2.000 330    -2.000   2
```

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4221100 CrF3            4.3630   13.2597                           0.00 0.00 0.00     108.9912
      4     1.000 211     3.000 270     2.000 330    -2.000   2
4321100 CrI3           32.1270  -20.4767                           0.00 0.00 0.00     432.7095
      4     1.000 211     3.000 380     2.000 330    -2.000   2
3021100 FECr204        24.8600    0.9016                           0.00 0.00 0.00     223.8366
      3     2.000 211     1.000 280    -4.000 330
3021101 MGCr204        39.8600  -12.0796                           0.00 0.00 0.00     192.2946
      3     2.000 211     1.000 460    -4.000 330
  21000 Cr METAL       34.3000  -32.2440                           0.00 0.00 0.00      51.9960
      2     1.000 210     2.000   1
3021102 Cr203          12.1250    3.3937                           0.00 0.00 0.00     151.9902
      3     2.000 211    -2.000 330    -1.000   2
2021102 Cr(OH)3 (A)     0.0000    0.7500                           0.00 0.00 0.00     103.0179
      3     1.000 211     1.000   2    -1.000 330
2021101 Cr(OH)3 (C)     7.1150   -1.7005                           0.00 0.00 0.00     103.0179
      3     1.000 211     1.000   2    -1.000 330
4121000 CrCL2          19.6660  -15.8676                           0.00 0.00 0.00     122.9020
      2     1.000 210     2.000 180
3021200 AG2CrO4       -14.0400   11.5548                           0.00 0.00 0.00     331.7296
      2     1.000 212     2.000  20
3021201 BACrO4         -6.3900    9.6681                           0.00 0.00 0.00     253.3236
      2     1.000 212     1.000 100
3021202 CS2CrO4        -7.5040    0.5541                           0.00 0.00 0.00     381.8044
      2     1.000 212     2.000 220
3021203 CS2Cr207      -22.8990   17.7793                           0.00 0.00 0.00     481.7986
      4     2.000 212     2.000 220     2.000 330    -1.000   2
3021204 CUCrO4          0.0000    5.4754                           0.00 0.00 0.00     179.5396
      2     1.000 212     1.000 231
3021205 K2CrO4         -4.2500   -0.0073                           0.00 0.00 0.00     194.1902
      2     1.000 212     2.000 410
3021206 K2Cr207       -18.1250   15.6712                           0.00 0.00 0.00     294.1844
      4     2.000 212     2.000 410     2.000 330    -1.000   2
3021207 LI2CrO4        10.8220   -4.8568                           0.00 0.00 0.00     129.8756
      2     1.000 212     2.000 440
3021208 MGCrO4         21.2600   -5.3801                           0.00 0.00 0.00     140.2986
      2     1.000 212     1.000 460
3021209 (NH4)2CrO4     -2.1900   -0.4046                           0.00 0.00 0.00     152.0702
      2     1.000 212     2.000 490
3021210 NA2CrO4         4.6100   -3.2618                           0.00 0.00 0.00     161.9731
      2     1.000 212     2.000 500
3021211 NA2Cr207       -5.3050    9.8953                           0.00 0.00 0.00     261.9673
      4     2.000 212     2.000 500     2.000 330    -1.000   2
3021212 PBCrO4        -10.2300   13.6848                           0.00 0.00 0.00     323.1936
      2     1.000 212     1.000 600
3021213 RB2CrO4        -5.8920    0.0968                           0.00 0.00 0.00     286.9292
      2     1.000 212     2.000 680
3021214 SRCrO4          2.4200    4.8443                           0.00 0.00 0.00     203.6136
      2     1.000 212     1.000 800
2021200 CrO3            1.2450    3.2105                           0.00 0.00 0.00      99.9942
      3     1.000 212     2.000 330    -1.000   2
3015000 CaCrO4          6.4400    2.2657                           0.00 0.00 0.00     156.0736
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      2     1.000 150     1.000 212
3036000 Hg2CrO4         0.0000   8.7031                  0.00 0.00 0.00   517.1736
      2     1.000 360     1.000 212
3***000 Tl2CrO4       -25.3100  12.0136                  0.00 0.00 0.00   524.7336
      2     2.000 870     1.000 212
8415004 TOBERMORITE           -120.619                   0.00 0.00 0.00   739.9900
      4     0.500 150     6.000 770    -1.500 002   -10.000 330
8450004 PHILLIPSITE               6.90                   0.00 0.00 0.00   287.3914
      6     0.500 550     0.500 410     1.000 030     3.000 770    -4.000 330    -3.000 002
6015000 MONOSULFATE            -73.822                   0.00 0.00      620.7250
      5     4.000 150     2.000 030     1.000 732    18.000 002   -12.000 330
6015001 ETTRINGITE             356.403                   0.00 0.00   0.001083.2410
      5     6.000 150     2.000 030     3.000 732    28.000 002    -2.000 330
      0
2812800 FE+3/FE+2   -10.0      13.032
      3     1.000 281    -1.000 280     1.000   1
4700020 KMNO4 -     176.6200  -127.8240                   -1. 3.0  0.0   118.9350
      4     1.000 470     4.000   2    -8.000 330    -5.000   1
4700021 KMNO4 -2    150.0200  -118.4400                   -2. 5.0  0.0   118.9350
      4     1.000 470     4.000   2    -8.000 330    -4.000   1
4914920 NO2/NO3     -43.76      28.57
      5     1.000 492    -1.000 491     2.000 330     2.000   1    -1.000   2
4904920 NH4/NO3     -187.055   119.077
      5    -1.000 490     1.000 492    -3.000   2    10.000 330     8.000   1
0600610 AS03/AS04   -30.015    19.444
      5     1.000  61     2.000   1     2.000 330    -1.000  60    -1.000   2
8908930 U+3/UO2+2   -10.03      0.420
      5     1.000 893     3.000   1     4.000 330    -1.000 890    -2.000   2
8918930 U+4/UO2+2   -34.43      9.216
      5     1.000 893     2.000   1     4.000 330    -1.000 891    -2.000   2
8928930 UO2+/UO2+2  -3.30       2.785
      3     1.000 893     1.000   1    -1.000 892
4714700 MN+3/MN+2   25.760     -25.507
      3     1.000 470    -1.000   1    -1.000 471
2302310 CU+1/CU+2   1.65        2.72
      3     1.000 231     1.000   1    -1.000 230
9009030 V+2/VO2+1   -35.33      18.38
      5     1.000 903     3.000   1     4.000 330    -1.000 900    -2.000   2
9019030 V+3/VO2+1   -44.23      22.61
      5     1.000 903     2.000   1     4.000 330    -1.000 901    -2.000   2
9029030 VO+2/VO2+1 -29.32       16.93
      5     1.000 903     1.000   1     2.000 330    -1.000 902    -1.000   2
7307320 HS-/SO4-2   -60.14      33.66
      5     1.000 732     9.000 330     8.000   1    -1.000 730    -4.000   2
3301404 CH4(GAS)    -61.0       41.08                                  16.0432
      4     1.000 140     8.000   1    10.000 330    -3.000   2
3301403 CO2(GAS)    -0.53       18.16                                  41.0100
      3     1.000 140     2.000 330    -1.000   2
3300021 O2(AQ) SATO             -45.54                                 31.9988
      3     2.000   2    -4.000 330    -4.000   1
3300022 O2(AQ) CALC 133.83      -85.98                                 31.9988
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      3     2.000   2    -4.000 330    -4.000   1
3600001 Hg (g)      -5.265    7.8708                                        200.5900
 0.00 2     0.500 360     1.000     1
3600002 Hg2 (g)     -13.87    14.963                                        401.1800
 0.00 2     1.000 360     2.000     1
3611400 Hg(CH3)2 (g -115.4    73.724                                        230.6594
 0.00 5     1.000 361     2.000 140    16.000
      1    20.000 330    -8.000   2
3601300 HgBr (g)    34.004    -16.79                                        280.4940
 0.00        2     0.500 360     1.000 130
3601800 HgCl (g)    40.098    -20.50                                        236.0430   0.00
      2     0.500 360     1.000 180
3602700 HgF (g)     60.916    -32.72                                        219.5884   0.00
      2     0.500 360     1.000 270
3603800 HgI (g)     25.264    -11.15                                        327.4945   0.00
      2     0.500 360     1.000 380
3611300 HgBr2 (g)   -14.35    18.47                                         360.3980   0.00
      4     1.000 361     2.000 130     2.000 330    -2.000   2
3612700 HgF2 (g)    0.0000    -0.38                                         238.5868   0.00
      4     1.000 361     2.000 270     2.000 330    -2.000   2
3613800 HgI2 (g)    -28.63    27.28                                         454.3990   0.00
      4     1.000 361     2.000 380     2.000 330    -2.000   2
8913305 KU6(OH)15+9 0        -17.229                    9. 0.0   0.0 1683.2846
      3     6.000 891    15.000   2   -15.000 330
3300023 O2(GAS)     136.63   -83.120
      3     2.000 002    -4.000 330    -4.000 001
2012000 CO3+/CO2+                33.01
      3     1.000 201     1.000 001    -1.000 200
8718700 Tl(OH)3/Tl+              48.0178
      5     1.000 871     2.000   1     3.000 330    -1.000 870    -3.000   2
7617600 HSeO3-1/HSe -78.17    44.866
      5     1.000 761     6.000   1     6.000 330    -1.000 760    -3.000   2
7627600 SeO4-2/HSe- -126.3    81.185
      5     1.000 762     8.000   1     9.000 330    -1.000 760    -4.000   2
7627610 SeO4/HSeO3  -48.095   36.319
      5     1.000 762     2.000   1     3.000 330    -1.000 761    -1.000   2
3613600 Hg(OH)2/Hg2 -63.59    42.987
      5     2.000 361     4.000 330     2.000   1    -1.000 360    -4.000   2
2102110 Cr+2/CrOH)2 -6.360    -2.947
      5     1.000 210     2.000   2    -1.000 211    -2.000 330    -1.000   1
2122110 CrO4/CrOH)2 -103.0    67.376
      5     1.000 212     6.000 330     3.000   1    -1.000 211    -2.000   2
      0
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13 ABSTRACT (200 words or less)

This MINTEQ user's manual was written to aid the user in applying the MINTEQ geochemical computer code to model aqueous solutions and the interactions of aqueous solutions with hypothesized assemblages of solid phases. The purpose of the user's manual is twofold: 1) to provide a basic understanding of how the MINTEQ computer code operates and the important principles that are incorporated into the code and 2) to instruct a user of the MINTEQ code on how to create input files to simulate a variety of geochemical problems. Chapters 2 through 8 are directed toward the user who has some experience with or wishes to review the principles important to geochemical computer codes. Also contained in these chapters is information on the methodology MINTEQ uses to incorporate these principles into the code. Chapters 9 through 11 are directed toward the user who wants to know how to create input data files to model various types of problems.

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